[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY, BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

Isolation of Partheniol, Parthenyl Cinnamate, and Other Constituents from Guayule Resin[1]

BY E. D. WALTER

In the program conducted in this Laboratory on the isolation and improvement of quality of rubber from guayule, *Parthenium argentatum* Gray, retting by aerobic microbiological decomposition to reduce the resin content received considerable attention. For the retting experiments it was of interest to know the chemical constituents of the resin and whether they were altered by retting. This paper describes some of the constituents isolated from the acetone extracts (considered to be resin) of the whole shrub, the foliage, the rubber from the unretted and the retted shrub and also from the resin exuded from the shrub.

A crystalline ester, which hyrolyzes to give cinnamic acid, and a crystalline sesquiterpene alcohol were obtained from the exuded resin and from an acetone extract of the rubber. Since the literature reveals no compounds identical with the ester or the alcohol, the name *partheniol* is proposed for the sesquiterpene alcohol and *parthenyl cinnamate* for the ester. Other constituents were obtained, in small amounts, which have not been definitely identified.

In 1911 Alexander[2] investigated the acetone-soluble constituents and ethereal oils derived from the guayule plant. He obtained an acid melting at 119°, which he thought belonged to the cinnamic series, and mentioned a private communication from R. Weil, who said he had found cinnamic acid in the saponification products of guayule resin. By prolonged steam distillation of the acetone extract of guayule wood, Alexander also obtained a crystalline substance melting at 127–28°, which he thought was a sesquiterpene alcohol. By distillation of the ethereal oils, he obtained two fractions. The first was characterized as pinene and the second was thought to be a sesquiterpene, $C_{15}H_{24}$, but efforts to identify it with any known sesquiterpene failed. Alexander mentioned that his sesquiterpene alcohol changed to a liquid on long standing. This tendency was also observed with *partheniol* and seems to be characteristic of the sesquiterpene tertiary alcohols described by Simonsen[3] under alcohols of unknown constitution, such as cedrol and ledol.

Experimental

Parthenyl Cinnamate.—The sticky balsam-like exudate from injured roots and bark of two-year old shrubs was collected with a penknife. The material was dissolved in ether and filtered, and the ether evaporated. At this stage the product resembled Canada balsam in appearance and had $n^{20}D$ 1.537, acid number 0.94, saponification number 34.5, iodine number 150. When 80% ethanol was added to this material until turbidity appeared and then allowed to stand for several days, a white crystalline substance separated. Recrystallization from acetone gave tetragonal crystals (Fig. 1), melting at 125–126°, with a yield of about 20% of the whole resin. This substance, named *parthenyl cinnamate,* is insoluble in water but soluble in organic solvents. Saponification of this substance with alkali in ethanol solution yields *partheniol* and cinnamic acid.

Anal. Calcd. for $C_6H_5CH{=}CHCO_2C_{15}H_{25}$: C, 81.81; H, 9.09; mol. wt., 352. Found: C, 81.97, 81.97; H, 8.97, 8.92; mol. wt. (Rast), 353 (saponification equivalent, 354); $[\alpha]^{24}D$ 61.6° ($CHCl_3$, c = 4.752).

This substance also was isolated from concentrated acetone extract of guayule rubber, supplied by the Rubber Laboratory, Navy Yard, Mare Island, California. After the extract had stood for about a month, crystals of parthenyl cinnamate (Fig. 1) were found throughout the sticky mass. On centrifuging, the yield of crystals contaminated with mother liquor was about 20% of the total. Pure crystals were obtained by clarification with Nuchar followed by recrystallization from acetone solution, the yield being about 5% of the extract.

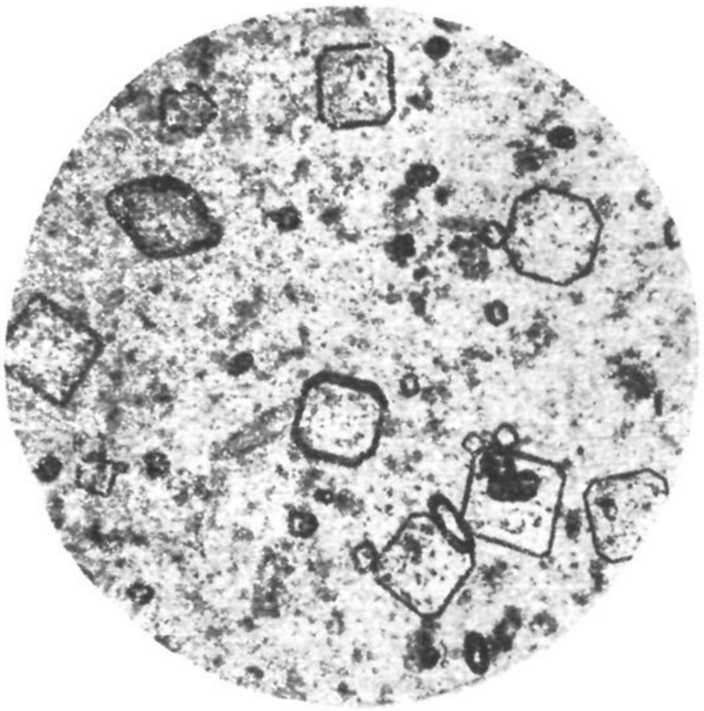

Fig. 1.—Parthenyl cinnamate (×30).

Partheniol.—The crystalline ester (0.56 g.) was saponified with 25 cc. of a saturated solution of potassium hydroxide in 95% ethanol. The excess alcohol was distilled, and the mixture was diluted with water and extracted with petroleum ether. The petroleum ether was removed, and the residue, when heated on the steam-bath in a beaker covered with a watch glass, yielded long silky crystals subliming and festooning the inside of the beaker. Repeated tufts of crystals were collected over a period of several days. The resublimed crystals (Fig. 2) melted at 131°; yield, 0.06 g. of partheniol from 0.56 g. of ester. It had a delicate terpene odor and was slightly soluble in hot water and very soluble in organic solvents. It may

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[1] Natural Rubber from Domestic Sources: Paper No. 1. Not copyrighted.

[2] P. Alexander, *Ber.*, **44**, 2320–2328 (1911).

[3] J. L. Simonsen, "The Terpenes," Cambridge University Press, London, 1932, Vol. II, pp. 585–596.

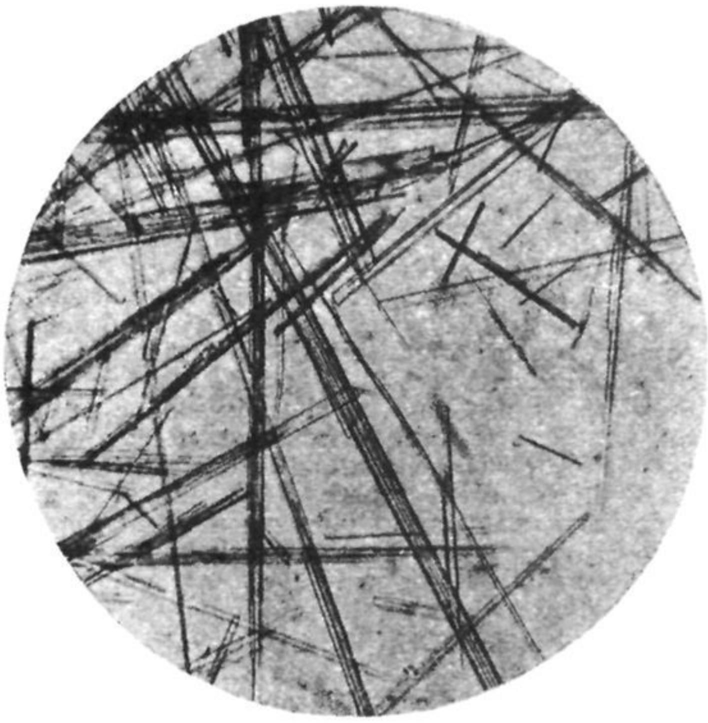

Fig. 2.—Partheniol (×100).

be obtained by steam distillation of the saponification mixture and crystallization in the aqueous distillate.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.08; H, 11.71; hydroxyl, 7.65; mol. wt., 222. Found: C, 81.17, 81.48; H, 11.39, 11.10; hydroxyl, 7.62, 7.65; mol. wt. (Rast), 233; $[\alpha]^{24}_D$ 88.7 ($CHCl_3$, c = 1.566).

Attempts to prepare the phenylurethan or the 3,5-dinitrobenzoate were unsuccessful. An attempt to dehydrate the alcohol to the hydrocarbon by shaking with 90% formic acid at room temperature resulted in the formation of the formate instead of the hydrocarbon.

The saponified fraction was acidified with hydrochloric acid. A tarry substance, as yet uncharacterized, separated and floated. This was partly filtered, and the filtrate was concentrated until crystals appeared on the surface on cooling. The crystals were separated and dissolved in 50% ethanol and clarified with Nuchar. When recrystallized and dried, they melted at 133°. The phenacyl derivative was prepared, and this melted at 140.5°. The conclusion that it was cinnamic acid was confirmed by an X-ray diffraction pattern from the powdered crystals, which agreed with that of known cinnamic acid.

Partheniol and cinnamic acid also were isolated from the saponification products of the acetone extracts of the rubber from retted shrubs, from whole shrubs, and from the foliage. The yield of partheniol from the rubber was about 2.5%, from the shrub about 2%, and from the foliage less than 1%, respectively, of the acetone extract. A small yield of partheniol was isolated from the unsaponifiable fraction of the mother liquor of the exuded resin from which parthenyl cinnamate had been crystallized.

Parthenyl Formate.—Partheniol, 0.7 g., was treated with 1.5 g. of 90% formic acid. The mixture was shaken and allowed to stand at room temperature for one hour. The acid was neutralized with sodium hydroxide, and the ester was extracted with ether. The alkali was removed by shaking the mixture with water and draining it off in a separatory funnel. The ether solution was dried with calcium chloride, and then the ether was evaporated. The product was a brown liquid, yield 0.6 g.; d^{25} 0.941; b. p. 215° (dec.) at 755 mm.; n^{25}_D 1.503.

Anal. Calcd. for $HCO_2C_{15}H_{25}$: C, 76.80; H, 10.40; mol. wt., 250. Found: C, 76.65, 76.49; H, 10.11, 9.93; mol. wt. (saponification equivalent), 250.

Crystallographic Optical Properties

When crystallized from the concentrated acetone extract from guayule rubber parthenyl cinnamate (Fig. 1) appears as tetragonal tablets and bipyramids. In convergent polarized light (crossed nicols), uniaxial interference figures are common. When crystallized from 80% ethanol the crystals appear more fragmented but the same interference figures are observed. The optic sign is positive. On fragments showing a well-centered uniaxial figure, $n\omega$ = 1.550. On fragments showing red interference color, $n\epsilon$ > 1.64 (the substance was soluble in the higher index liquids available).

Sublimed crystals of partheniol appear as very long orthorhombic lathlike prisms (Fig. 2). In parallel polarized light (crossed nicols) the extinction is parallel; the elongation is negative. All crystals extinguish rather sharply and no clear interference figures are found in convergent polarized light. Lengthwise $n\alpha$ = 1.538; across the elongation $n\gamma$ = 1.590; $n\beta$ = indet.

Wax-like Substance.—The air-dried foliage (1500 g. of leaves and flowering stems) was ground in a Ball and Jewell mill to $^1/_{16}$-inch size and extracted with warm acetone in a Soxhlet type extractor for thirty-two hours. The extract was cooled before being concentrated and on standing overnight deposited fine crystalline material. Recrystallization from either ethanol or acetone gave tiny white crystals melting at 76°; yield, 3.73 g. or about 0.25% of the foliage or about 3 to 4% of the acetone extract (resin). It was soluble in organic solvents, but insoluble in water and in concentrated sulfuric acid. It dissolved slowly in fuming sulfuric acid, forming a brown solution. It did not absorb bromine.

Anal. Found: C, 80.18; H, 13.25; saponification number, 74.4; mol. wt. (Rast), 597.

The same substance was obtained in lower yields from acetone extracts of the whole shrub and from rubber from both retted and unretted shrubs. Attempts to identify it with any known substance have not been successful.

Volatile Oil.—Steam distillation of acetone extract of guayule rubber gave a volatile oil, n^{25}_D 1.4938, $[\alpha]^{25}_D$ −17.92°, b. p. 244–245° at 750 mm. Attempts to prepare a nitrosochloride or a bromide of this material failed. It is probably a mixture of sesquiterpenes.

Products of Vacuum Distillation of Acetone-Extracted Resin.—Distillation of 650 g. of resin in a Fenske column yielded about 80 g. of liquid between 28° and 17 mm. and 162° and 26 mm. A greenish solid was collected between 170° and 25 mm. and 202° and 4 mm. The major part of this fraction proved to be cinnamic acid.

The liquid fraction was redistilled in a short Fenske column at a pressure of about 1 mm. No constant boiling temperature was attained, but cuts were made between 70 and 78°, 78 and 81°, and 82 and 90°. The lower boiling fraction had n^{24}_D 1.4850 and $[\alpha]^{22}_D$ −10.5° (1-dm. tube). The intermediate fraction had n^{24}_D 1.4952 and $[\alpha]^{22}_D$ −9.17° (1-dm. tube); b. p. 244–245° at 755 mm. The higher boiling fraction had n^{24}_D 1.4995 and $[\alpha]^{22}_D$ −6.84; b. p. 246–247° at 755 mm. *Anal.* of the higher boiling fraction: Calcd. for $C_{15}H_{24}$: C, 88.23; H, 11.76; found: C, 87.59, 87.40; H, 11.17, 11.09. Since no partheniol was obtained in these distillates and cinnamic acid was obtained, it appears that the alcohol was dehydrated in the process and appeared in these fractions as the sesquiterpene, $C_{15}H_{24}$, the higher boiling fraction being the least contaminated.

Discussion

Since parthenyl cinnamate, partheniol, and cinnamic acid were isolated from the whole shrub, from the foliage, and from rubber from both the retted and the unretted shrub, it is obvious that the acetone extracts from all of these are qualitatively similar. The foliage extract, of course, contains more chlorophyll and more wax-like material than that from the whole shrub or from the rubber. No wax-like material was found in the exuded resin, and since this is practically free of chlorophyll it might be considered as the true guayule resin. About 20% of the exuded resin was parthenyl cinnamate. The acetone extract of the rubber also yielded roughly 20% of crude parthenyl cinnamate.

Acknowledgment.—The author is indebted to the Rubber Laboratory, Navy Yard, Mare Island, California, for a supply of acetone extract of guayule rubber and to Dr. C. L. Ogg and assistants of the Microanalytical Laboratory for the analyses reported.

Summary

1. *Partheniol*, a new sesquiterpene alcohol, and *parthenyl cinnamate* were isolated from guayule resin, and some of their properties, including crystallographic optical properties, are described.

2. A crystalline waxlike substance and several fractions of volatile oils, probably sesquiterpenes, were prepared from acetone extracts of whole shrub, guayule foliage, and guayule rubber.

3. Retting of the shrub appears to make no change in the relative proportions of the constituents isolated from the resin.

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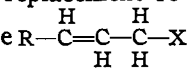
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XIV. The Hydrolysis of Butenyl Chlorides[1]

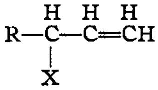
BY WILLIAM G. YOUNG AND LAWRENCE J. ANDREWS

Recent work[2] on nucleophilic replacement reactions of allylic systems of the type



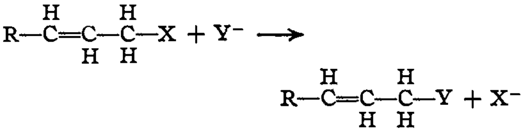
$R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}X$

or

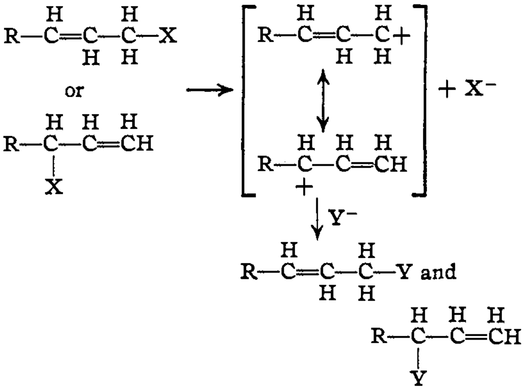


$R{-}\underset{X}{\overset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}H$

indicates that bimolecular or S_N2 reactions produce unrearranged products (Equation 1). Unimolecular or S_N1 type reactions, involving an unfree carbonium ion intermediate, lead to a mixture of allylic isomers (Equation 2)

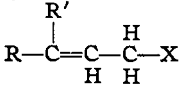
(1) 

$$R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}X + Y^- \longrightarrow R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}Y + X^-$$

(2) 

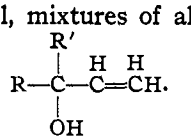
$$\begin{matrix} R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}X \\ \text{or} \\ R{-}\underset{X}{\overset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}H \end{matrix} \longrightarrow \left[\begin{matrix} R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{+} \\ \updownarrow \\ R{-}\underset{+}{\overset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}H \end{matrix}\right] + X^- \xrightarrow{Y^-} R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}Y \text{ and } R{-}\underset{Y}{\overset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}H$$

The relative contributions of types (1) and (2) in a given reaction are readily influenced by the experimental conditions. With this in mind it was desirable to examine critically the apparently conflicting reports in the literature concerning the hydrolysis of alkenyl halides.[3] For example, halides of the type



$R{-}\overset{R'}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}X$

are reported to give primary alcohol, mixtures of alcohols or the pure allylic isomer,



$R{-}\underset{OH}{\overset{R'}{C}}{-}\overset{H}{C}{=}\overset{H}{C}H$.

Although reaction (1) would account for the production of pure normal product and reaction (2) would give a mixture due to the formation of a resonating carbonium ion intermediate, neither (1) nor (2) should give a pure secondary alcohol from a pure primary halide.

The present investigation has been undertaken to show that under controlled conditions it is possible to account for the products of hydrolysis of the butenyl chlorides[4] in terms of the mechanisms given above. Reaction conditions were varied from those favorable to S_N1 type hydrolysis to those suitable for a bimolecular type (S_N2) reaction of the organic halide with hydroxide ion. From a consideration of the composition of the alcohols produced in these reactions (Table I) it was possible to compare the relative contributions of the S_N1 and S_N2 type processes to the hydrolysis of the two halides. The correctness of the estimated contributions of the mechanisms to these hydrolyses has been demonstrated by an investigation of the kinetics of the reactions.

The Products of Hydrolysis of the Butenyl Chlorides.—The reactions with silver oxide were studied to determine the composition of

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[1] This paper was presented before the Division of Organic Chemistry of the American Chemical Society, Memphis, April, 1942.

[2] (a) (XIII) Roberts, Young and Winstein, THIS JOURNAL, **64**, 1725 (1942); (b) Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[3] (a) Claisen and Tietze, *Ber.*, **59**, 2344 (1926). (b) Claisen, *J. prakt. Chem.*, [2] **105**, 65 (1922). (c) Prévost, *Ann. chim.*, [10] **10**, 113 (1928). (d) Meisenheimer and Link, *Ann.*, **479**, 211 (1930). (e) Petrov, *J. Gen. Chem.* (U. S. S. R.), **11**, 713 (1941).

[4] In order to avoid complications arising from thermal rearrangement of the starting material the pure primary and secondary butenyl chlorides have been used rather than the corresponding bromides.