reflux period of six hours resulted in a lowered yield of phenolic product.

2,3-Dimethoxy-2-hydroxybiphenyl.—A mixture of 500 mg. of 2-(2′,3′-dimethoxyphenyl)-cyclohexanone, 5 ml. of triethylbenzene, and 1.0 g. of 5% palladium–charcoal catalyst[5] was heated under reflux for one hour. The warm solution was filtered and the catalyst washed with warm benzene. The organic solution was extracted with one 25-ml. and one 15-ml. portion of Claisen alkali. The Claisen solution was washed with benzene, and the benzene added to the organic solvents. The combined organic solution was extracted with three 15-ml. portions of Claisen alkali, and the combined Claisen solution was washed with 40 ml. of pentane. The alkaline solution was diluted with 100 ml. of water. A 40-ml. portion of concentrated hydrochloric acid was added and neutralization was completed with carbon dioxide (Dry Ice). After chilling, the crystalline product was removed by filtration and air dried. The yield of phenol, m. p. 102–104°, was 225 mg. Recrystallization from cyclohexane gave a colorless sample, m. p. 103–104.5°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.22; H, 6.07.

Acknowledgment.—The authors are indebted to Miss Sarah H. Miles for carrying out the analyses reported here.

Summary

The synthesis of 2-(2′,3′-dimethoxyphenyl)-2-(β-ethoxyethyl)-cyclohexanone is described.

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[5] "Organic Syntheses," 26, 77 (1946).

[CONTRIBUTION FROM THE KERCKHOFF LABORATORIES OF BIOLOGY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY AND THE EMERGENCY RUBBER PROJECT, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

Chemical Investigation in Guayule. II. The Structure of Partheniol, A Sesquiterpene Alcohol from Guayule

BY A. J. HAAGEN-SMIT AND C. T. O. FONG[1]

In studies conducted in this Laboratory on the constituents of guayule, *Parthenium argentatum, Gray*, it was found that cold alcohol extracted from the plant a cinnamate of an optically active sesquiterpene alcohol previously isolated by Alexander.[2] The yield of the alcohol from the plant was approximately 0.03%. Later, the same ester was obtained by chromatographic adsorption of guayule extracts on silicic acid. Further studies showed that guayule resin obtained from Mexico as a by-product of guayule rubber refining would serve as a convenient source of this alcohol, yielding as much as 0.3% of the desired substance.

The physical constants of this alcohol and its cinnamate are listed below and are compared with those given by Alexander[2] and by Walter.[3]

Parthenyl cinnamate: empirical formula, $C_{24}H_{30}O_2$,[4,2] $C_{24}H_{32}O_2$[3]; m. p. 125–126°[4,2,3]; molecular weight by saponification of ester, 355[4], 354.[3]

Partheniol: empirical formula, $C_{15}H_{24}O$,[4,2] $C_{15}H_{26}O$[3]; m. p. 127–128°,[4,2] 131°[3]; mol. wt. 215,[4] 222[2]; $[\alpha]^{26}\text{D}$ 116.5° ($CHCl_3$, *c* 1.29%),[4] $[\alpha]^{24}\text{D}$ + 88.7° ($CHCl_3$, *c* 1.566%)[3]; parthenyl *p*-phenylazobenzoate, m. p. 162.5–164°[4]; parthenyl 3,5-dinitrobenzoate, m. p. 143–144°.[4]

Our data for the alcohol are in agreement with those of Alexander and the empirical formula $C_{15}H_{24}O$ for the alcohol was substantiated throughout this work. Also the melting point of partheniol repeatedly recrystallized from different solvents agrees with that of Alexander. The chromatographic separation of the phenylazobenzoate showed only traces of compounds other than the partheniol derivative. The presence of isomeric forms of partheniol might explain the melting point of 131° found by Walter[3] since we have observed that heating partheniol with alcoholic potassium hydroxide resulted in a raise of melting point to 132–132.5°. Similar observations were made in preparing a maleic anhydride addition compound.

Catalytic hydrogenation of the alcohol indicated the presence of two double bonds. The absorption spectrum of partheniol, together with the failure of partheniol to form an adduct with maleic anhydride or to be reduced by sodium in alcohol, indicates that the two double bonds are not conjugated.

The relative ease of dehydration with potassium bisulfate confirms the presence of an alcoholic hydroxyl group and indicates that the hydroxyl group is probably tertiary. The failure of esterification with phthalic anhydride under conditions described by Ruzicka, *et al.*,[5] as well as the failure to form a xanthate indicated that partheniol is a tertiary alcohol.[6]

Dehydration of partheniol with potassium bisulfate resulted in the formation of a mixture of isomeric hydrocarbons, $C_{15}H_{22}$, which we shall call dehydroparthenene.[7] These hydrocarbons contain three double bonds, which physical and chemical methods show are not conjugated.

Dehydrogenation of dehydroparthenene with sulfur gave blue S-guaiazulene which was identified by its 1,3,5-trinitrobenzene addition product, its picrate and its trinitrotoluene addition prod-

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[1] Present address, Lederle Research Laboratories, Pearl River, N. Y.

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

[3] Walter, THIS JOURNAL, **66**, 419 (1944).

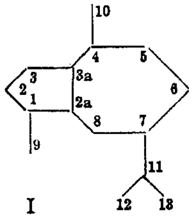
[4] Data of Haagen-Smit and Fong.

[5] Ruzicka, Pontalti and Balas, *Helv. Chim. Acta*, **6**, 858 (1923).

[6] Feigl, "Spot Tests," Nordemann Publishing Co., New York, N. Y., 1937, p. 251.

[7] Conforming to sesquiterpene nomenclature: parthenene is $C_{15}H_{24}$.

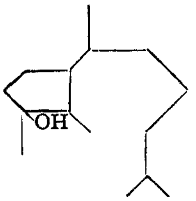
uct. The adsorption spectrum of the S-azulene obtained from partheniol correspond with those reported for S-guaiazulene by Willstaedt[8] and by Plattner.[9] Dehydration of dehydroparthenene with selenium gives a violet azulene. This behavior is similar to that shown by the dehydrogenation of a crystalline sesquiterpene alcohol, guaiol obtained from the wood of *Guaiacum officinale* (family *Zygophyllacae*).[10] These data show that the carbon skeleton of partheniol is that of 1,4 - dimethyl - 7 - isopropyl - decahydrocyclopentacycloheptene (I).



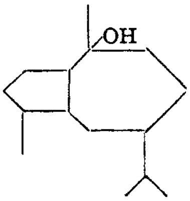
I

Tetrahydropartheniol, $C_{15}H_{28}O$, is formed by hydrogenating both double bonds of partheniol. Dehydration of tetrahydropartheniol with potassium bisulfate gives dihydroparthenene, $C_{15}H_{26}$, a hydrocarbon containing one double bond. In the ozonization of dihydroparthenene formaldehyde was formed, indicating the presence of a methylene group. Since the double bond in this methylene group arose from the removal of the hydroxyl group in tetrahydropartheniol, we may conclude that the hydroxyl group in partheniol is situated on a carbon atom to which a methyl group is attached.

If the hydroxyl group were located at carbon atom 7 or 11 dehydration of tetrahydropartheniol to dihydroparthenene would have given a mixture of isomers yielding acetone and formaldehyde upon ozonization. As no trace of acetone could be detected in the ozonization products, only two structures are possible for tetrahydropartheniol. They are shown in II and III.

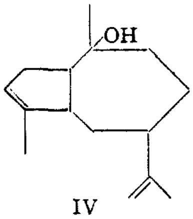


II

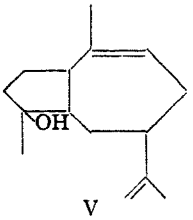


III

The position of the hydroxyl group at carbon atom 1 or carbon atom 4 is confirmed by the results of ozonization experiments on partheniol, since a neutral product, $C_{14}H_{22}O_4$, containing an aldehyde and two methyl ketone groups was obtained. The presence of formaldehyde among the volatile oxidation products demonstrated that one of the double bonds is exocyclic and present in a methylene group. The oxidation of the double bond located in the isopropenyl group explains the formation of formaldehyde and one of the methyl ketone groups. The other double bond has given rise to the aldehyde and second methyl ketone group. This limits the position of the second double bond to one adjoining a methyl group and one not connected with the bridge between the 5 and 7 membered ring. The fourth oxygen in $C_{14}H_{22}O_4$ is present as in the original tertiary hydroxyl group. This leaves out of the numerous possible isomers only the following two structures for partheniol.



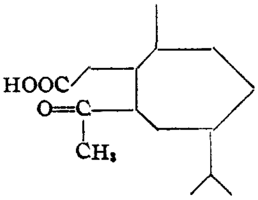
IV



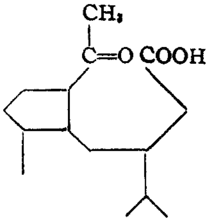
V

These structures are in harmony with the absence of conjugation of the double bonds in partheniol and its dehydration product dehydroparthenene. To secure a possible check of the exact position of the hydroxyl group the dicarboxylic acid, which was formed from the ozonization of dihydroparthenene followed by hypobromite oxidation, was treated with acetic anhydride according to Blanc's method.[11]

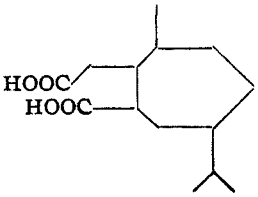
In the removal of the hydroxyl group from tetrahydropartheniol, a mixture of isomers is formed, which upon ozonization gives rise to a ketone, a diketone and a keto acid (VI or VIII) or keto aldehyde. On hypobromite oxidation of the keto acid, a dicarboxylic acid is formed which would be, in the case of structure II, a substituted glutaric acid (VII), and in the case of structure III, a substituted pimelic acid (IX). With acetic anhydride, ketone formation was not detected, indicating the presence of a glutaric acid derivative rather than a pimelic acid derivative. Also, our



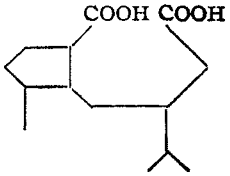
VI



VIII



VII



IX

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[8] Willstaedt, *Ber.*, **68**, 333 (1935).

[9] Plattner, *Helv. Chim. Acta*, **24**, 283E (1941).

[10] Ruzicka and Haagen-Smit, *ibid.*, **14**, 1104 (1931).

[11] Blanc, *Compt. rend.*, **144**, 1356 (1907).

analytical data show that an anhydride rather than a ketone was formed. These facts indicate that the hydroxyl group in partheniol is attached to carbon atom 1, as shown in structure V.

Experimental[12]

Isolation of Partheniol.—Twenty-five gallons of crude resin was extracted three times with five-gallon portions of ether and twice with seven-gallon portions of a 5:2 ether–methanol mixture. After the removal of the solvents from the extract, the ether-soluble portion of the guayule resin was saponified with *N* alcoholic solution of sodium hydroxide for three hours at a bath temperature of 90°. After neutralization and extraction with ether, the residue (about five gallons) was distilled at 0.01 mm. pressure. Approximately two liters of material boiling below 150° collected. Redistillation through a short helix-packed column fitted with a variable take-off still head yielded 1.2 liters of viscous oil boiling at 100–125° at 0.01 mm. pressure. This distillate was then diluted slightly with petroleum ether and inoculated with a few crystals of partheniol. After standing for several days, this solution became a solid mass of partheniol crystals.

These were recrystallized from petroleum ether to constant melting point: 150 g. of purified crystalline partheniol, m. p. 127–128°, was obtained. This melting point stayed constant after recrystallization from petroleum ether, from acetone and from benzene as well as after sublimation.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.77, 81.73; H, 10.92, 10.98.

Attempt at Reduction of Partheniol with Sodium and Alcohol.—Two grams of partheniol in 10 ml. of amyl alcohol was heated in a 40-ml. flask at a bath temperature of 135° for six and one-quarter hours. Sodium (4.5 g.) was gradually added; at periodic intervals, more amyl alcohol was introduced until all the sodium had reacted. The residue was recrystallized twice from low-boiling petroleum ether; the substance melted at 132–132.5°.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.85; H, 11.06.

Reaction of Partheniol with Maleic Anhydride.—The reaction of partheniol with maleic anhydride or ethyl maleate dissolved in benzene and refluxed for ten hours gave no adduct. The recovered partheniol melted at 129.5°, no depression with original partheniol.

Absorption Spectrum of Partheniol.—The absorption spectrum of a solution of 1.76 mg. of partheniol in 100 ml. of absolute alcohol was determined with the Beckman photoelectric spectrophotometer. The spectrum did not show any characteristic maxima or minima within the range of the spectrophotometer.

Parthenyl *p*-Phenylazobenzoate.—To 2 g. of partheniol in 15 ml. of dry pyridine 2.4 g. of *p*-phenylazobenzoyl chloride in 20 ml. of anhydrous benzene was added. The reaction mixture was heated at a bath temperature of 90° for half an hour and worked up in the usual manner. The residue was recrystallized first from a mixture of benzene and petroleum ether, then from acetone.

One gram of this benzoate dissolved in a mixture of 10 ml. of benzene and 50 ml. of petroleum ether (85–100°) was chromatographed on a silicic acid–celite column (2:1) 4.5 cm. × 20 cm., which had been initially washed with 250 ml. of petroleum ether. The column was developed with 400 ml. of petroleum ether (85–100°) and post-washed with 50 ml. of 30–60° petroleum ether. The chromatogram showed two very faint bands near the top. The main zone *ca.* 10 cm. below the top was cut out from the extruded column and was recovered by eluting with ether; after recrystallizing three times from acetone, m. p. 163–164°.

Anal. Calcd. for $C_{28}H_{32}O_2N_2$: C, 78.47; H, 7.53; N, 6.54. Found: C, 78.42; H, 7.53; N, 6.66.

Parthenyl 3,5-Dinitrobenzoate.—A solution of approximately 150 mg. of partheniol and an equal amount of 3,5-dinitrobenzyl chloride in a mixture of 2 ml. of dry benzene and 5 ml. of anhydrous pyridine was gently refluxed for 0.75 hour. The reaction mixture was worked up according to Reichstein.[13] The turbid solution was allowed to stand in the refrigerator for several days: the crystals formed were recrystallized from acetone and washed with alcohol, m. p. 143–144°.

Anal. Calcd. for $C_{22}H_{26}N_2O_6$: C, 63.75; H, 6.31; N, 6.76. Found: C, 63.88, 63.97; H, 6.61, 6.51; N, 6.67, 6.90.

Dihydropartheniol.—A 5.04-g. sample of partheniol dissolved in 55 ml. of absolute ethanol was hydrogenated with approximately 2 g. of Raney nickel as catalyst at 25° and 760 mm. pressure.

The rate of hydrogenation was fairly rapid for the first fifteen hours, decreasing rapidly thereafter. The hydrogenation was terminated after the required amount of hydrogen for one double bond was taken up. After the removal of the Raney nickel and the alcohol, the remaining oil was distilled at 92–102° at 0.1 mm.; a total of 3.5 g. of dihydropartheniol was obtained. The dihydropartheniol gave the constants: n^{26}_{D} 1.5035, $d^{23.6}_{4}$ 0.9614; calcd. M_D for $C_{15}H_{26}O$ with one double bond and one hydroxyl group is 68.15; found 68.5; *p*-phenylazobenzoate, m. p. 121.5–122.5°.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.05; H, 11.96.

Dehydroparthenene.—A mixture of 5 g. of partheniol and 3.5 g. of fused potassium acid sulfate was refluxed at a bath temperature of 180–190° for one-half hour. Extraction was carried out with ether and the recovered oil was distilled twice over potassium. In the second distillation at 60–65° and 0.1 mm., 1.1 g. of dehydroparthenone was obtained: n^{26}_{D} 1.15120, $d^{23.6}_{4}$ 0.9194. Calcd. M_D is 65.67 calcd. for three double bonds; found 66.04.

Anal. Calcd. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.90; H, 11.15.

Dehydrogenation of Dehydroparthenene.—Fifteen grams of crude dehydroparthenene was heated with 4.7 g. of sulfur at a pressure of 30–50 mm. and a bath temperature of 180–185°, for three hours.[14] The blue azulene which was formed was distilled directly from the reaction flask. The fraction obtained at 70–100° and 10–15 mm. was 7 g. The distillate was taken up in petroleum ether and the azulene was extracted with 85% phosphoric acid following the procedure of Ruzicka, *et al.*[15] The crude azulene distilled at 140–150° (bath temperature) and 0.05 mm. The yield based on crude parthenene is 1.7%. The purification was carried out as indicated by Plattner and St. Pfau[16] by converting the azulene to its trinitrobenzene addition compound.

The addition compound was decomposed and the azulene liberated through chromatographic adsorption on an aluminum oxide column. The trinitrobenzene forms a zone at the top of the column while the azulene is less strongly adsorbed. After development with petroleum ether the azulene was eluted with a mixture of 1:1 benzene–petroleum ether. A trinitrobenzene addition product was again prepared and the cycle of the decomposition and the regeneration of the azulene was repeated. The final product was distilled under reduced pressure. Approximately 125 mg. of the purified blue azulene was obtained.

Anal. Calcd. for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.93; H, 9.24.

The addition products of the azulene with picric acid, trinitrobenzene and trinitrotoluene were prepared following the methods of Plattner and St. Pfau.[16]

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[12] All melting points are corrected; microanalysis by Dr. G. Oppenheimer and G. Swinehart.

[13] Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

[14] Melville, THIS JOURNAL, **55**, 2462 (1933).

[15] Ruzicka and Rudolph, *Helv. Chim. Acta*, **19**, 858 (1936).

[16] Plattner and St. Pfau, *ibid.*, **20**, 224 (1937).

Picrate, m. p. 120–121°. *Anal.* Calcd. for $C_{21}H_{21}N_3O_7$: C, 59.01; H, 4.95; N, 9.83. Found: C, 58.79; H, 4.88; N, 10.09.

Trinitrobenzene addition compound, m. p. 150–151°. *Anal.* Calcd. for $C_{21}H_{21}N_3O_6$: C, 61.34; H, 5.14; N, 10.21. Found: C, 61.61; H, 4.99; N, 10.12.

Trinitrotoluene addition compound, m. p. 88–89°. *Anal.* Calcd. for $C_{22}H_{23}N_3O_6$: C, 62.11; H, 5.45; N, 9.88. Found: C, 62.30; H, 5.74; N, 10.06.

The melting points found in the literature are: picrate m. p. 120–121°, trinitrobenzene compound 150–151.5° and trinitrotoluene compound 88–89°.[10,17]

Absorption Spectrum of the S-Azulene.—The absorption spectrum of the S-azulene in hexane, with a concentration of 3.62 mg. per 10 ml., was determined with a Beckman photoelectric spectrophotometer using a slit width of 0.02 to 0.3 mm. The spectrum was characterized by three maxima at 603, 659 and 735 mμ and undulations at 557, 582, 630 and 698 mμ.

Reported for S-guaiazulene are strong bands at 604, 663, 736 mμ and weak bands at 557, 581, 633 and 697 mμ.[18,19]

Tetrahydropartheniol.—32.8 g. of partheniol was hydrogenated at room temperature and at a pressure slightly above atmospheric in 200 ml. of glacial acetic acid with 0.4 g. of platinum dioxide as a catalyst. After removal of the catalyst and the solvent, the hydrogenated product distilled at 70–85° at 0.01 mm.: n^{25}_D 1.4820, $d^{25.4}_4$ 0.9342; *MR calcd., 68.60 for one hydroxyl group; found,* 68.47.

Anal. Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.16; H, 12.72.

Dihydroparthenene.—A mixture of 38.5 g. of tetrahydropartheniol and 24 g. of fused powdered potassium bisulfate was heated for forty-five minutes at a bath temperature of about 160°. After washing the ether extract with dilute sodium hydroxide and with water until neutral, the hydrocarbon was distilled twice over potassium. The dihydroparthenene had the *following constants:* b. p. (0.02 mm.) 59–60°; n^{25}_D 1.4880; d^{25}_4 0.9025; *MR* calcd. 66.6 for one double bond; found, 65.9.

Anal. Calcd. for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.31; H, 12.83. Microhydrogenation: Found: uptake 1.0 mole H_2, calcd. for $C_{15}H_{26}$.

Ozonization of Partheniol.—Five grams of partheniol was ozonized in glacial acetic acid. The ozonide was decomposed by hydrogenation in 1:1 acetic acid–ether with a *platinum catalyst (Adams). The reaction mixture* was cooled in an ice–salt-bath during the first phase of the hydrogenation in order that a secondary reaction of "acid rearrangement" of the ozonide would not occur to any appreciable extent. The hydrogenation was later allowed to proceed at room temperature till the required amount of hydrogen was taken up. A test for formaldehyde on the volatile products with dimedon reagent was positive, while a test for acetone with *p*-nitrophenylhydrazine was negative. From the ozonized products was separated a neutral fraction, by making the solution alkaline and extracting with ether. An acid fraction was obtained by acidifying the alkaline solution and extracting with ether. A qualitative test for methyl ketone in the neutral fraction was positive; a qualitative test for aldehyde with Schiff reagent was also positive.

The amount of acid fraction was negligible. A greater portion of the neutral fraction was not distillable. By distilling at 0.6 mm. and 98–100°, 0.5 g. of the neutral fraction was collected with the *following constants:* n^{24}_D 1.4762; d^{24}_4 1.0624.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.01; for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.74; H, 8.69. Micro-Zerewitinoff: Found: 0.9 mole act. H and 1.8 moles carbonyl, when calcd. for $C_{14}H_{22}O_4$. Methyl ketone determination. Found: 1.9 moles CH_3CO group, calcd. for $C_{14}H_{22}O_4$.

Quantitative Ozonization of Partheniol and of Dihydroparthenene.—Following the procedure and using the apparatus described by Grignard, Doeuvre and Escourrou,[20,20a] a 1.5-g. sample of partheniol was ozonized in 25 ml. of acetic acid (30% water) at 17° for forty minutes (ozone concn. 1.24 g./hr.). Decomposition of the ozonide was carried out by adding 50 ml. of water and heating at 100° for three hours. A suspension of mercuric oxide in water was then added and the reaction mixture was heated in a boiling water-bath for one hour. The wash-bottles did not contain formaldehyde when tested with dimedon. The amount of carbon dioxide formed by oxidation of the formic acid present was 180 mg. or 60% of the theoretical amount if one exocyclic double bond were present.

Following the same procedure 0.85 g. of dihydroparthenene was ozonized in 25 ml. of acetic acid containing 30% water for forty minutes (O_3 concentration 1.24 g./hr.). The amount of formaldehyde which was precipitated was negligible; the quantity of carbon dioxide after oxidation of the formic acid with mercuric oxide was 111 mg. or 65% of the theoretical if one exocyclic double bond were present. This result was confirmed by ozonizing 0.4 g. of dihydroparthenene in carbon tetrachloride. The ozonide was decomposed by adding 10 ml. of water and heating on a boiling water-bath. A test with dimedon for formaldehyde on the volatile products was positive; a test for acetone with *p*-nitrophenylhydrazine was negative.

Ozonization of Dihydroparthenene and Reduction of Ozonides.—An 18.2-g. sample of dihydroparthenene in 40 ml. of glacial acetic acid was ozonized at about 15° for three hours. To decompose the ozonide, 18 g. of zinc dust suspended in a small amount of water was slowly added; the reaction temperature was kept at 50–70° for approximately one hour. A test for peroxides was made with titanic sulfate and dilute sulfuric acid; no peroxides were found. After the removal of the excess zinc and zinc salts, the acetic acid solution was neutralized with dilute potassium hydroxide and the neutral solution was extracted with ether. An acid fraction was obtained by acidifying the ether-extracted aqueous phase with dilute sulfuric acid and extracting with ether. Fractionation of neutral fraction at 0.125 mm. gave the following fractions: 68–78°, 6.4 g.; 78–93°, 1.4 g.; 93–108°, 2.4 g.; 108–120°, 2.8 g.

Anal. Calcd. Fr. b. p. (0.125 mm.) 68–78°. Found: C, 83.83; H, 12.51. Fr. b. p. (0.125 mm.) 78–93°. Found: C, 77.56; H, 11.36. Fr. b. p. (0.125 mm.) 93–108°. Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. For $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 75.17; H, 11.37.

Ozonization of Dihydroparthenene and Oxidation of Ozonides.—A 10.5-g. sample of dihydroparthenene was ozonized in 20 ml. of glacial acetic acid for 1.5 hours (1.45 g. O_3/hour). Since a maximum yield in acid fraction was desired, the ozonide was decomposed with a 5–7% solution of hydrogen peroxide, heating in a water-bath for an hour. The excess hydrogen peroxide was removed by heating for half an hour in the presence of a few mg. of platinum black. The mixture was concentrated in order to remove the excess acetic acid. A neutral and acid fraction were obtained by making the concentrate basic and acidic, respectively, and extracting with ether. The total acid fraction obtained was 2.5 g.; the neutral fraction 4.5 g. Distillation of the acid fraction at 0.1 mm. gave the following fractions: 176–190°, 0.65 g.; 190–210°, 0.5 g.

Anal. Fraction b. p. (0.1 mm.,) 176–190°, calcd. for $C_{15}H_{26}O_3$: C, 70.82; H, 10.30; for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 66.51; H, 9.70.

Oxidation of Acid Fractions with Sodium Hypobromite.—Fraction b. p. (0.1 mm.) 176–190° was treated with

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[17] St. Pfau and Plattner, *Helv. Chim. Acta*, **19**, 870 (1936).

[18] Willstaedt, *Ber.*, **68**, 333 (1935).

[19] Susz, St. Pfau and Plattner, *Helv. Chim. Acta*, **20**, 469 (1937).

[20] Grignard, Doeuvre and Escourrou, *Compt. rend.*, **177**, 669 (1923).

[20a] Escourrou, *Bull. soc. chim.*, [4] **43**, 1088 (1928).

sodium hypobromite (1.7 g. of sodium hydroxide, 2 g. of bromine in 23 ml. of water) for two hours. The excess sodium hypobromite was decomposed with a small amount of sodium bisulfite. After removing the neutral fraction containing bromoform, the alkaline solution was acidified with sulfuric acid and an acid fraction was extracted with ether. The major portion (0.39 g.) distilled at 0.1 mm. and a bath temperature of 190–200°.

Anal. Fr. b. p. (0.1 mm.) 190–200° after redist.: calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44 (dicarboxylic acid). Found: C, 64.34; H, 9.52.

Reaction of Dicarboxylic Acid with Acetic Anhydride.[5]—A mixture of 0.3 g. of dicarboxylic acid obtained from fraction b. p. (0.1 mm.) 190–200° and 0.5–0.7 ml. of acetic anhydride was heated in a sealed tube for half an hour at 240° (bath temperature).

After removal of the acetic anhydride, the reaction mixture was distilled under high vacuum. A fraction of approximately 50 mg. which distilled at 0.01 mm. pressure and a bath temperature of 200–210° was obtained.

Anal. Calcd. for $C_{14}H_{24}O_4$ (acid): C, 65.60; H, 9.44. For $C_{14}H_{22}O_3$ (anhydride): C, 70.55; H, 9.30. For $C_{13}H_{20}O$ (ketone): C, 80.35; H, 11.41. Found: C, 68.17; H, 9.17.

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Summary

The structure of partheniol, a sesquiterpene alcohol isolated from guayule, *Parthenium argentatum, Gray,* has been determined.

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Resin Acids. III. The Isolation of Dextropimaric Acid and a New Pimaric-type[1] Acid, Isodextropimaric Acid

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The history of the discovery and isolation of dextropimaric[2] acid parallels that of levopimaric[2] acid by virtue of one property common to both acids, namely, the insolubility of their crystalline sodium salts. In other physical and chemical properties, they are significantly different. Dextropimaric acid is not susceptible to oxidation by air or isomerization by heat or dilute mineral acid, whereas levopimaric acid is relatively sensitive to both changes.

Previous methods of isolation of dextropimaric acid depended on fractional crystallization as its insoluble sodium salt from mixtures of resin acids such as "galipot"[3] or on recrystallization after oxidation of the more susceptible acids.[4] We have obtained a fraction containing dextropimaric acid and related acids by removal of the two-double-bond abietic-type acids by reaction with maleic anhydride after acid isomerization. The unreacted acids were separated from the maleic anhydride adduct by precipitation from aqueous alkaline solution by adjustment of the *p*H to 6.2.[5] Ultraviolet absorption spectra showed the absence of two-double-bond abietic-type acids in this fraction.

Further fractionation of this mixture has not only given relatively large amounts of dextropimaric acid but also yielded a new pimaric-type acid. When this resin acid fraction was dissolved in acetone and treated with butanolamine, an insoluble salt was obtained and recrystallized to constant rotation $[\alpha]^{20}\mathrm{D}$ 0°. When the salt was decomposed with mineral acid, the resin acid was obtained which was crystallized first from alcohol and water as thin plates and finally as needles after standing in the mother liquor; $[\alpha]^{24}\mathrm{D}$ 0°; m. p. 162–164°; neutral equivalent 302. The yield was 8% of the total oleoresin acids of *Pinus palustris.* The physical constants indicated a new resin acid. The isolation of formaldehyde as its "dimedon" derivative, m. p. 190–191°, on ozonolysis at −60° and of pimanthrene as its trinitrobenzolate,[6] m. p. 158–160°, on dehydrogenation with palladium–carbon catalyst at 330° proved it to be a pimaric-type acid. The homogeneity of the acid was proved by the preparation and purification of the methyl ester, m. p. 61.5–62°, and the butanolamine salt, $[\alpha]^{24}\mathrm{D}$ 0°, and the regeneration of the acid with the same physical constants. The ultraviolet absorption spectrum, like that of dextropimaric acid, showed no maximum, indicating the absence of a conjugated double bond system.[7] This new pimaric-type acid has been termed isodextropimaric acid.

Dextropimaric acid was isolated from the acids regenerated from the residual salts, after that of isodextropimaric acid was separated, by crystallization first from acetone and then from glacial acetic acid in 4% yield with rotation, $[\alpha]^{24}\mathrm{D}$ + 79°, m. p. 213–215°. The isolation of dextro-

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(1) We wish to designate by this term that type of resin acid which yields pimanthrene (1,7-dimethylphenanthrene) upon complete dehydrogenation, and that has the gem configuration of methyl and vinyl groups at C-7. Evidence for this will be shown in a subsequent publication: G. C. Harris and T. F. Sanderson, Resin Acids. IV. THIS JOURNAL, **70**, 2081 (1948). The abietic-type acids are those that yield retene (1-methyl-7-isopropylphenanthrene) upon complete dehydrogenation and have an isopropyl or isopropylidene group at C-7.

(2) These words have purposely been written as one word since the compounds are not stereoisomers as the prefixes *levo-* and *dextro-* would imply.

(3) A. Vesterberg, *Ber.*, **20**, 3248 (1887).

(4) E. Knecht and E. Hibbert, *J. Soc. Dyers Colourists*, **38**, 221 (1922).

(5) A method developed by W. P. Campbell of this Laboratory.

(6) L. Ruzicka and L. Sternbach, *Helv. Chim. Acta*, **23**, 124 (1940).

(7) V. N. Krestinskii, S. S. Malevskaya, N. F. Komshilov and E. V. Kazeeva, *J. Applied Chem.* (*U. S. S. R.*), **12**, 1840 (1939).