inserted at 210°, darkening immediately). Plattner[18] reports a m.p. 232–234° for the dioxime of cycloundecane-1,6-dione.

A solution of 198 mg. of the neutral material, 0.40 g. of semicarbazide hydrochloride and 0.60 g. of sodium acetate was refluxed for 20 minutes. The white solid was filtered but it was too insoluble in all common solvents to permit recrystallization; yield 114 mg. (35%), m.p. 220.0–220.5° dec. (darkening 190°). Plattner[18] reports a m.p. 218° for the disemicarbazone of cycloundecane-1,6-dione.

Anal. Calcd. for $C_{13}H_{24}O_2N_6$ (296.37): C, 52.68; H, 8.16; N, 28.36. Found: C, 52.94; H, 8.16; N, 28.36.

Hydrogenation of Acetolysis Product.—A mixture of 2.08 g. of the *cis* solvolysis product, 40 ml. of glacial acetic acid and 0.12 g. of platinum oxide was hydrogenated at 45 pounds pressure. After 1 hour, the reaction ceased and the uptake amounted to exactly 1 mole equivalent of hydrogen. The catalyst was filtered, the filtrate diluted with water, extracted with pentane and the extract washed with water and sodium bicarbonate solution. The pentane was removed under reduced pressure and the product distilled in short-path molecular type still at a block temperature of 90–95° (15–20 mm.); yield 1.71 g. (81.3%), $n^{25}\text{D}$ 1.4819. The infrared spectrum of the material was identical with that of an authentic sample of bicyclo[5.4.0]undecane.

Benzsuberane.[18]—A mixture of 5.00 g. (31.2 mmoles) of benzsuberone,[18,25] 3.7 ml. (63 mmoles) of 85% hydrazine hydrate and 25 ml. of diethylene glycol was heated under gentle reflux for 30 minutes. The reaction mixture was cooled, 4.16 g. of 85% sodium hydroxide was added and the mixture then heated at a bath temperature of 210° and the volatile components allowed to distil. The mixture then was heated under reflux until the evolution of nitrogen ceased (40 minutes). The cooled reaction mixture and distillate were combined, poured into water and extracted with pentane. The extracts were washed with water, concentrated on the steam-bath and the residue distilled through a screen packed column, b.p. 108–109° (22 mm.), yield 3.87 g. (84.8%), $n^{25}\text{D}$ 1.5386 (lit.[18] b.p. 99.8–100.0° (13 mm.), $n^{20}\text{D}$ 1.5520).

Anal. Calcd. for $C_{11}H_{14}$ (146.22): C, 90.35; H, 9.65. Found: C, 90.34; H, 9.77.

Bicyclo[5.4.0]undecane.—A mixture of 2.00 g. of benzsuberane, 30 ml. of glacial acetic acid and 0.30 g. of platinum oxide was hydrogenated at pressure of 45 pounds. The reaction ceased when 3 mole equivalents of hydrogen had been adsorbed. The mixture was processed and distilled as described for the hydrogenation of *cis* acetolysis product; yield 1.77 g. (85%), $n^{25}\text{D}$ 1.4818 (lit.[18] $n^{20}\text{D}$ 1.4845).

Anal. Calcd. for $C_{11}H_{20}$ (152.27): C, 86.76; H, 13.24. Found: C, 87.03; H, 13.09.

Kinetic Measurements.—A solution (250 ml.) of the tosylate (approx. 0.05 M) and sodium acetate (approx. 0.1 M) in anhydrous acetic acid was placed in a constant temperature bath and allowed to come to thermal equilibrium for 30 minutes before any aliquots were withdrawn. Each kinetic point was determined by withdrawing an aliquot with a 5-ml. calibrated automatic pipet, diluting with approximately 40 ml. of anhydrous acetic acid and titrating potentiometrically using a model G Beckman *p*H meter. The electrodes employed were silver chloride platinum wire and a glass electrode. The solutions were titrated with 0.0545 M *p*-toluenesulfonic acid monohydrate in anhydrous acetic acid with the stoichiometric amount of acetic anhydride added to react with the water of crystallization present in the toluenesulfonic acid. The data for one run are given in Table II.

TABLE II

ACETOLYSIS OF *trans*-9-DECALYLCARBINYL TOSYLATE AT 90.03 ± 0.03°

Time, sec.	Titer, ml.	10^{1} k, sec.$^{-1}$
0	8.73	..
16,200	8.55	2.83
31,800	8.30	2.60
77,400	7.78	2.87
99,000	7.56	2.92
120,600	7.37	2.68
163,800	7.01	2.92
185,400	6.84	2.92
207,000	6.67	3.07
268,800	6.28	2.92
348,900	5.84	2.95
	4.29	..
	Average	2.87 ± 0.10

BERKELEY 4, CALIFORNIA

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[25] J. W. Cook, R. Philip and A. R. Sommerville, *J. Chem. Soc.*, 164 (1948).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, R. J. REYNOLDS TOBACCO CO.]

Flue-cured Tobacco. II. Neophytadiene

BY R. L. ROWLAND

RECEIVED APRIL 8, 1957

An unsaturated hydrocarbon, neophytadiene, has been isolated from aged flue-cured tobacco leaf and has been shown to be 3-methylene-7,11,15-trimethyl-1-hexadecene. Neophytadiene also has been obtained in small amounts from the dehydration of phytol. The dehydration of phytol has produced different olefins depending upon the acidity of the dehydration media.

In a continuation of our study of the ether-soluble materials extracted from aged flue-cured tobacco,[1] we have investigated the hydrocarbon fraction. The hydrocarbons were isolated by chromatography using silicic acid and alumina. The saturated hydrocarbons were separated from the unsaturated hydrocarbons by crystallization from acetone. The saturated hydrocarbons, which made up 0.06–0.1% of the dry weight of the tobacco leaf, appeared to be identical with those studied by Chibnall, *et al.*,[2] who found a mixture of straight-chain hydrocarbons containing an odd number of carbon atoms ranging from $C_{25}H_{52}$ to $C_{33}H_{68}$. The unsaturated hydrocarbon, which also constituted 0.06–0.1% of the dry weight of the tobacco leaf, has been named neophytadiene. Our studies have shown that neophytadiene is 3-methylene-7,11,-15-trimethyl-1-hexadecene (I).

The infrared absorption of neophytadiene, Fig. 1, showed absorption at 6.27 μ, indicating conju-

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[1] R. L. Rowland, P. H. Latimer and J. A. Giles, THIS JOURNAL, **78**, 4680 (1956).

[2] A. C. Chibnall, S. H. Piper, A. Pollard, E. F. Williams and P. N. Sahai, *Biochem. J.*, **28**, 2189 (1934).

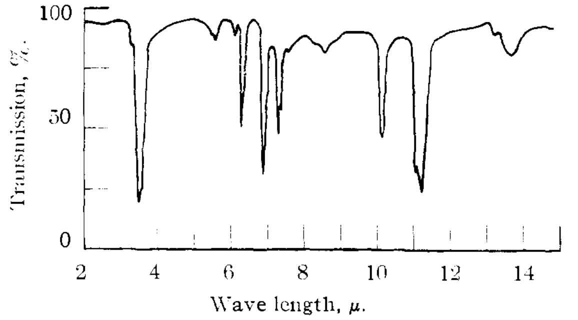
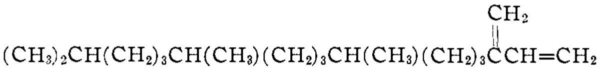


Fig. 1.—Infrared absorption spectrum of neophytadiene, oil.

gated double bonds; at 7.25 and 7.32 μ, indicating an isopropyl group; at 10.1 and 11.2 μ, indicating a grouping $R_1R_2C{=}CH_2$; and at 11.1 μ indicating $R_3CH{=}CH_2$. The maximum absorption in the ultraviolet at 224.5 mμ, log ε 4.4, indicated two conjugated double bonds. Quantitative determination of unsaturation by catalytic reduction gave equivalent weights of 135 and 146 in agreement with two double bonds in a 20-carbon compound. These results, combined with the similarity of infrared spectrum and refractive index of the hydrogenation product with that of phytane,[3] suggested the structure



$$(CH_3)_2CH(CH_2)_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3\overset{\overset{CH_2}{\|}}{C}CH{=}CH_2$$

I

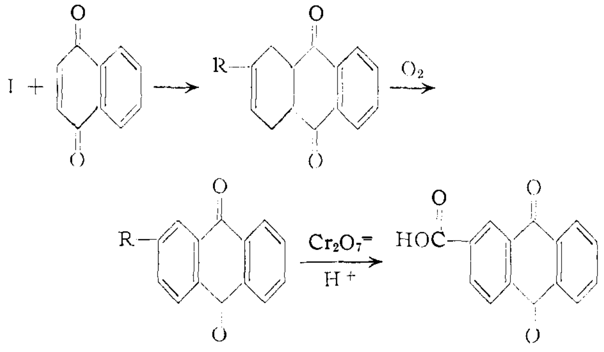
Ozonization of neophytadiene followed by reductive hydrolysis of the ozonide gave formaldehyde as the only steam-volatile product. From the reductive hydrolysis of the ozonide, the ether-soluble material which was not steam volatile was oxidized by potassium permanganate in acetone. The product was an acid whose elemental analyses and neutral equivalent indicated it to be $C_{17}H_{34}O_2$ or $C_{16}H_{32}O_2$ or a mixture of these acids. From direct oxidation of neophytadiene by potassium permanganate in acetone, an acid was obtained which, from its analyses, appeared to be $C_{17}H_{34}O_2$, presumably

$$(CH_3)_2CHCH_2CH_2CH_2CH(CH_3)\text{-}$$
$$CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2COOH$$

as expected from the oxidation of I.

The Diels–Alder reaction of neophytadiene with maleic anhydride produced an adduct whose elemental analyses and saponification equivalent agreed well with $C_{24}H_{40}O_3$. Hydrolysis of the anhydride gave the dicarboxylic acid whose elemental analyses and neutral equivalent agreed with $C_{24}H_{42}O_4$.

The Diels–Alder reaction of neophytadiene with 1,4-naphthoquinone followed by air oxidation of the adduct produced the only solid derivative which we have obtained from neophytadiene. The air-oxidized adduct, $C_{30}H_{40}O_2$ (IV), was further oxidized by dichromate in sulfuric acid to anthraquinone-2-carboxylic acid.



IV

R = 4,8,12-trimethyltridecyl-.

The similarity of the structures of neophytadiene and phytadiene prompted a brief study of phytadiene. Phytadiene has been obtained by the dehydration of phytol on distillation,[4] by heating phytol with phthalic anhydride in benzene,[5] by heating phytol with oxalic acid in dioxane[6] and by removing the elements of hydrogen bromide from phytyl bromide.[7] The phytadiene obtained by dehydration of phytol using oxalic acid has been shown by ozonization studies to be a mixture of 3,7,11,15-tetramethyl-1,3-hexadecadiene (II) and 3,7,11,15-tetramethyl-2,4-hexadecadiene (III) with the predominant material considered to be II.[8]

$$(CH_3)_2CH(CH_2)_3CH(CH_3)(CH_2)_3CH(CH_3)\text{-}$$
$$CH_2CH_2CH{=}C(CH_3)CH{=}CH_2$$

II

$$(CH_3)_2CH(CH_2)_3CH(CH_3)(CH_2)_3CH(CH_3)\text{-}$$
$$CH_2CH{=}CHC(CH_3){=}CHCH_3$$

III

For comparative purposes, we have prepared phytadiene by the oxalic acid dehydration procedure. The reaction mixture was purified by chromatography to give a 30% yield of olefin, a 33% recovery of phytol and a 30% yield of a material which from its infrared spectrum was considered to be the half-ester of phytol and oxalic acid. The phytadiene which we obtained by this procedure showed an infrared spectrum identical with the infrared spectrum of phytadiene (kindly furnished us by Prof. Karrer) and very similar to that of neophytadiene. The spectra of this phytadiene, which we have called phytadiene A, and of neophytadiene differed only in that neophytadiene lacked the absorption bands at 6.2, 9.25 and 10.38 μ found in phytadiene A and neophytadiene showed much less absorption at 6.07 μ than did phytadiene A. Both possessed the absorption bands at 11.1 and 11.2 μ which we interpreted as due to $R_3CH{=}CH_2$ and $R_1R_2C{=}CH_2$. The phytadiene A which we obtained by this procedure showed a maximum absorption in the ultraviolet at 227 mμ, whereas previous reports have indicated the maximum absorption of phytadiene at 232[8] and 230 mμ.[9]

The Diels–Alder reaction of phytadiene A with 1,4-naphthoquinone and subsequent air oxidation

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(3) J. Pliva and N. A. Sörensen, *Acta Chim. Scand.*, **4**, 846 (1950); J. S. Sörensen and N. A. Sörensen, *ibid.*, **3**, 939 (1949).

(4) R. Willstätter and F. Hocheder, *Ann.*, **354**, 205 (1907).

(5) R. Willstätter, E. W. Mayer and E. Huni, *ibid.*, **378**, 73, 109 (1910).

(6) P. Karrer, H. Simon and E. Zbinden, *Helv. Chim. Acta*, **27**, 313, 317 (1944).

(7) L. I. Smith, H. E. Ungnade, H. H. Hoehn and S. Wawzonek, *J. Org. Chem.*, **4**, 311 (1939).

(8) P. Karrer, A. Kugler and H. Simon, *Helv. Chim. Acta*, **27**, 1006 (1944).

(9) F. Bader, *ibid.*, **34**, 1632 (1951).

were accomplished. Chromatography of the reaction mixture allowed separation into unreacted olefin and two substituted anthraquinones, obtained in a 5:1 ratio. The substituted anthraquinone obtained in smaller amounts was identical with the compound obtained by the same reaction sequence using neophytadiene. Since oxidation of the anthraquinone obtained from neophytadiene produced anthraquinone-2-carboxylic acid, the substituted anthraquinone must be 2-(4′,8′,12′-trimethyl-tridecyl)-anthraquinone and the phytadiene A must have contained a small amount of 3-methylene-7,11,15-trimethyl-1-hexadecene (I) identical with neophytadiene.

The substituted anthraquinone obtained in the larger amount from the Diels–Alder reaction of phytadiene A and 1,4-naphthoquinone followed by air oxidation was isomeric with that obtained in smaller amount. The substituted anthraquinone is presumed to be 1-(3′,7′,11′-trimethyldodecyl)-2-methylanthraquinone and the major portion of phytadiene A is presumed to be 3,7,11,15-tetramethyl-1,3-hexadecadiene (II) as previously reported.[8]

In the process of purifying phytol, preliminary to carrying out the oxalic acid dehydration, the commercial sample of phytol[10] was chromatographed on alumina. From a 10-g. sample of phytol, 170 mg. of olefin was eluted with hexane. The infrared absorption, ultraviolet absorption and refractive index of this olefin were identical with those of neophytadiene. This olefin, which we have called phytadiene B, was allowed to react with 1,4-naphthoquinone and the adduct was air oxidized to give the substituted anthraquinone identical with the substituted anthraquinone obtained from neophytadiene and, in smaller amount, from phytadiene A.

The dehydration of phytol using phthalic anhydride[5] gave us negligible yields of olefin. When, however, a strong acid catalyst (*p*-toluenesulfonic acid) was added to the reaction mixture, an 80% yield of olefin (phytadiene C) was obtained. Phytadiene C differed markedly from phytadienes A and B. The infrared and ultraviolet absorption suggested that phytadiene C is 3,7,11,15-tetramethyl-2,4-hexadecadiene (III).

It is obvious that the phytadiene obtained from dehydration of phytol can have a number of structures and that the material formed depends upon the acidity of the dehydration mixture. In the absence of the acid catalyst and in the tobacco leaf during the processes of curing and aging, the least substituted diene I would be expected to form from the dehydration of phytol. In the oxalic acid dehydration of phytol, the presence of acid would be expected to result in formation of the dienes which are more highly substituted (II, III); our studies indicate the formation of a mixture of I, II and III. With *p*-toluenesulfonic acid in benzene, phytol is dehydrated to give III or an isomer in which the double bonds are shifted yet further into the molecule.

The identity of neophytadiene with phytadiene B and with the olefin present in small amounts in phytadiene formed by oxalic acid dehydration shows that neophytadiene is 3-methylene-7,11,15-trimethyl-1-hexadecene (I). This material is expected to have resulted from breakdown of the phytol (*ex* chlorophyll) in the tobacco leaf.

Acknowledgments.—We are indebted to Mr. John J. Whalen for the infrared spectra and to Mr. R. H. Cundiff and Mr. B. N. Sullivan, Jr., for certain analytical determinations.

Experimental[11]

Isolation of Neophytadiene.—The extraction and partial separation of the hexane-soluble materials of aged flue-cured tobacco were reported in the first paper of this series.[1] Fraction 1 of chromatogram 1 and similar fractions obtained by large scale chromatograms of the same tobacco leaf extract have been investigated. Using a silicic acid column, 6 in. (152 cm.) (diam.) × 20 in. (508 cm.), 140 g. of hexane-soluble material was chromatographed. The material eluted by hexane (7.4 g.) consisted of saturated and unsaturated hydrocarbons. The saturated hydrocarbons were separated by crystallization from acetone. From 5.0 g. of mixed hydrocarbon fraction and 60 ml. of acetone, 2.3 g. of saturated hydrocarbon crystallized at room temperature and a small amount of material also separated on cooling the filtrate to −27°. The material soluble in acetone at −27°, 2.4 g., was chromatographed on alumina using hexane.

The unsaturated hydrocarbon was a free-flowing colorless oil, $n^{26}\mathrm{D}$ 1.4604, which was not optically active. *Anal.* Calcd. for $C_{20}H_{38}$: C, 86.25; H, 13.75. Found: C, 86.08; H, 13.74. The ultraviolet absorption showed a maximum at 224.5 mμ, log ϵ 4.4 with a weaker maximum at 279 mμ, log ϵ 2.8.

Quantitative Reduction.—Quantitative reduction in ethanol using palladium-on-charcoal catalyst gave equivalent weights of 135 and 146. Considering a molecular weight of 278, the molecule would contain 2.06, 1.9 double bonds. The saturated hydrocarbon isolated in 80% yield was an oil, $n^{25}\mathrm{D}$ 1.4422. *Anal.* Calcd. for $C_{20}H_{42}$: C, 85.03; H, 14.97. Found: C, 85.21; H, 14.88.

Ozonization.—Ozonization of 374 mg. of neophytadiene was accomplished in ethyl acetate at ice-bath temperature. The ozonide was reduced with zinc dust and the volatile compounds were steam distilled into 250 ml. of 2 *N* hydrochloric acid saturated with 2,4-dinitrophenylhydrazine. The precipitate, after washing with 2 *N* hydrochloric acid and with water, was chromatographed on silicic acid giving 180 mg. (32%) of material showing the infrared absorption of formaldehyde dinitrophenylhydrazone. After recrystallization from hexane, the product melted at 162–164° and gave no depression of m.p. on mixing with an authentic sample of formaldehyde dinitrophenylhydrazone. Similar isolation of the dinitrophenylhydrazone obtained from ozonization of 172 mg. of olefin in chloroform gave 160 mg. (62%) of formaldehyde dinitrophenylhydrazone.

The non-volatile products from the ozonization in ethyl acetate were extracted with ether. The ethereal extract was washed with water and was concentrated. The residue, 300 mg., was oxidized at room temperature with 1.0 g. of potassium permanganate in 20 ml. of acetone. After 20 hours, the reaction mixture was treated with 70 ml. of 10% sulfuric acid and 1.5 g. of sodium bisulfite. The mixture was extracted with 100 ml. of ether. The ethereal extract was washed with four 30-ml. portions of water and was dried over anhyd. sodium sulfate. Concentration under reduced pressure left a residue of 260 mg. Purification by chromatography on silicic acid gave acid Y (100 mg.), eluted by benzene. Acid Y showed an infrared spectrum essentially the same as that of acid Z obtained by permanganate oxidation of neophytadiene. *Anal.* Calcd. for $C_{17}H_{34}O_2$: C, 75.49; H, 12.67; neut. equiv., 270. Calcd. for $C_{16}H_{32}O_2$: C, 74.97; H, 12.58; neut. equiv., 256. Found: C, 74.67; H, 12.50; neut. equiv., 302.

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(10) Obtained from Organic Research Chemicals, Bucks, England.

(11) All melting points were determined on a Fisher–Johns melting point apparatus. All chromatographic separations were made by the use of liquid or flowing chromatograms, in which the separated materials were obtained by use of eluents in a graded series. Elemental analyses were by Micro-Tech Laboratories, Skokie, Ill., and the Clark Microanalytical Laboratory, Urbana, Ill.

Permanganate Oxidation of Neophytadiene.—A mixture of 1.7 g. of potassium permanganate, 0.425 g. of neophytadiene and 40 ml. of acetone was allowed to stand at room temperature for 18 days. To the mixture were added 70 ml. of 10% sulfuric acid and 2 g. of sodium bisulfite. The mixture was extracted with ether, the ethereal extract was washed with water, dried and concentrated at reduced pressure. The residue was purified by chromatography using silicic acid. A carboxylic acid Z, 260 mg., was eluted with benzene. The infrared absorption, essentially the same as acid Y, showed the presence of an isopropyl group (7.25, 7.31 μ) and a methylene chain (13.6 μ); $n^{25.5}\text{D}$ 1.448; no detectable optical activity. *Anal.* Calcd. for $C_{17}H_{34}O_2$: C, 75.49; H, 12.67; neut. equiv., 270.4. Found: C, 75.27; H, 12.77; neut. equiv., 268, 273.

Diels–Alder Reaction with Maleic Anhydride.—The reaction of neophytadiene with maleic anhydride was accomplished in ether at room temperature. The reaction product was separated from unreacted olefin by chromatography on silicic acid from which the anhydride was eluted by benzene. The adduct was an oil, $n^{26}\text{D}$ 1.4786, with no detectable optical activity. On cooling to −27°, the oil crystallized. *Anal.* Calcd. for $C_{24}H_{40}O_3$: C, 76.57; H, 10.71; sapn. equiv., 188. Found: C, 76.28; H, 10.80; sapn. equiv., 192. The adduct did not show the infrared absorption at 10.1, 11.1 and 11.2 μ related to the presence of $=CH_2$.

From a run in which the Diels–Alder reaction mixture was washed with 2 portions of water, chromatography of the ether-soluble material allowed separation into unreacted olefin (24%), anhydride adduct (41%) and the carboxylic acid formed by hydrolysis of the anhydride (35%).

Hydrolysis of the Diels–Alder Adduct.—A mixture of 0.31 g. of adduct and 9 ml. of 5% potassium hydroxide solution was warmed gently for 0.5 hour. The alkaline mixture was extracted with ether and was then acidified with 1 *N* hydrochloric acid. The acid mixture was extracted with ether. The ethereal extract was washed with water and was concentrated under reduced pressure to a residue of 0.24 g. Purification was accomplished by chromatography on silicic acid, from which the acid was eluted by ether. The product was a viscous oil, $n^{25}\text{D}$ 1.482. *Anal.* Calcd. for $C_{24}H_{42}O_4$: C, 73.05; H, 10.73; neut. equiv., 197. Found: C, 72.84; H, 10.33; neut. equiv., 209, 214.[12]

Diels–Alder Reaction with 1,4-Naphthoquinone.—A mixture of 0.22 g. of neophytadiene, 0.22 g. of 1,4-naphthoquinone and 5 ml. of ethanol was heated under reflux for 4 hours. A solution of 0.05 g. of potassium hydroxide in 8 ml. of ethanol was added and air was bubbled through the mixture for three hours. The mixture was concentrated under reduced pressure. The residue was extracted with 20 ml. of hexane and the hexane extract was chromatographed using silicic acid. The oxidized adduct (IV, 0.051 g.) was eluted by carbon tetrachloride. After crystallization from methanol at −27°, the product melted at 47.5–49.5°. *Anal.* Calcd. for $C_{30}H_{40}O_2$: C, 83.29; H, 9.32; mol. wt., 432.6. Found: C, 83.22; H, 9.40; mol. wt., 410.

Dichromate Oxidation of IV.—IV, 0.025 g., was dissolved in 0.9 ml. of concd. sulfuric acid. To the solution were added 0.9 ml. of water and 0.3 g. of powdered sodium dichromate. The mixture was heated at 80–90° for 2 hours. After 16 hours, the mixture was diluted with 20 ml. of water and was extracted with two 15-ml. portions of benzene and three 15-ml. portions of ether. The benzene–ether extracts were washed with water and were concentrated under reduced pressure. The residue was chromatographed on silicic acid from which the acid (0.011 g., 80%) was eluted by ether. The acid melted at 292–293° and the melting point was not changed by crystallization from an alcohol–water mixture. Anthraquinone-2-carboxylic acid has been reported to melt at 291–292°.[13] *Anal.* Calcd. for $C_{15}H_8O_4$: C, 71.43; H, 3.19. Found: C, 71.28; H, 3.52.

Phytadiene A.—The dehydration of phytol was attempted by the procedure of Karrer, Simon and Zbinden.[6] The reaction product was not distilled but was purified by chromatography using silicic acid. An olefin (0.3 g., eluted by hexane), unreacted phytol (0.4 g., eluted by benzene) and a material (D), whose infrared absorption indicated that it contains an ester grouping and a carboxylic acid grouping (0.4 g., eluted by ether), were obtained from dehydration of 1.2 g. of phytol. The olefin fraction was chromatographed again using alumina, giving 0.27 g. of phytadiene, $n^{25}\text{D}$ 1.4636, $[\alpha]^{25}\text{D}$ +2.1° (1.03 g. in 100 ml. of chloroform). The infrared absorption of this material was identical with the infrared absorption of phytadiene, kindly furnished us by Professor P. Karrer. The ultraviolet absorption showed a maximum at 227 mμ, log ϵ 4.3.

The half-ester D was heated under nitrogen in an oil-bath maintained at 160° for one hour. The reaction mixture was extracted with hexane and the hexane extract was chromatographed on alumina. A 25% yield of olefin was noted. The infrared spectrum indicated a mixture of phytadiene A and phytadiene C, $n^{24}\text{D}$ 1.4719. The olefin showed a broad ultraviolet maximum between 225 and 232 mμ, log ϵ 4.12.

Phytadiene B.—Phytol (10 g.),[10] was purified by chromatography using alumina. The hexane eluate contained 0.17 g. of colorless oil, $n^{25}\text{D}$ 1.4604, which showed an infrared spectrum identical with that of neophytadiene. The ultraviolet absorption showed a maximum at 225 mμ, log ϵ 4.23.

Phytadiene C.—The dehydration of phytol using phthalic anhydride in benzene[5] gave us a negligible yield of olefin, as determined by chromatography of the reaction mixture on alumina. When the reaction was repeated with the addition of 25 mg. of *p*-toluenesulfonic acid (for 1.2 g. of phytol, 1.0 g. of phthalic anhydride and 40 ml. of benzene) an 80% yield of olefin was isolated by chromatography using silicic acid. The olefin showed a maximum absorption in the ultraviolet at 235 mμ, log ϵ 4.38; $n^{25}\text{D}$ 1.4704, $[\alpha]^{25}\text{D}$ −9.58° (2.86 g. in 100 ml. of chloroform). The infrared absorption no longer showed bands at 10.1, 11.1 and 11.2 μ (as in phytadiene A and B) but showed strong absorption at 10.38 μ indicative of a *trans*-CH=CH grouping.

Reaction of Phytadiene A with 1,4-Naphthoquinone.—A mixture of 156 mg. of phytadiene A, 175 mg. of 1,4-naphthoquinone and 15 ml. of ethanol was heated under reflux for three hours. To the cooled solution was added 6 ml. of ethanol containing 0.07 g. of potassium hydroxide. Air was bubbled through the mixture for 2 hours after which time the ethanol was removed under reduced pressure. The residue was extracted with two 15-ml. portions of hexane and the hexane extract was separated by chromatography on silicic acid into (1) 68 mg. of olefin (infrared spectrum similar to that of the starting phytadiene A except that the band at 11.1 μ is now stronger than the band at 11.2 μ) eluted by hexane, (2) 71 mg. of oxidized adduct E eluted by carbon tetrachloride and (3) 15 mg. of oxidized adduct F eluted by carbon tetrachloride. Recrystallization of E from methanol at −27° gave 50 mg. of yellow solid, m.p. 57–59°. *Anal.* Calcd. for $C_{30}H_{40}O_2$: C, 83.29; H, 9.32. Found: C, 83.39; H, 9.46. Recrystallization of F from methanol at −27° gave 8 mg. of yellow solid, m.p. 47.5–49°, which showed no depression of m.p. upon mixing with the oxidized adduct obtained from reaction of the neophytadiene with 1,4-naphthoquinone. The infrared spectrum of F was identical with that of the oxidized adduct obtained from neophytadiene.

Reaction of Phytadiene B with 1,4-Naphthoquinone.—A mixture of 88 mg. of phytadiene B, 144 mg. of 1,4-naphthoquinone and 15 ml. of ethanol was heated under reflux for 3 hours. To the cooled mixture was added 6 ml. of ethanol containing 0.07 g. of potassium hydroxide. Air was bubbled through the mixture for 2 hours after which time the ethanol was removed under reduced pressure. The residue was extracted with two 15-ml. portions of hexane and the hexane extract was chromatographed on silicic acid giving separation into 60 mg. of unreacted olefin, eluted by hexane, and 20 mg. of oxidized adduct eluted by carbon tetrachloride. The infrared spectrum of the oxidized adduct, m.p. 46–47°, was identical with that of the oxidized adduct obtained from neophytadiene and that of the oxidized adduct F obtained from phytadiene A.

WINSTON-SALEM, N. C.

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[12] R. H. Cundiff and P. C. Markunas, *Anal. Chem.*, **28**, 792 (1956). This dibasic acid gave two inflections as expected on titration with tetrabutylammonium hydroxide in pyridine.

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