the histochemical methods. The phosphoric acid esters, on the other hand, dissolve readily in buffered solutions, and were found to be more satisfactory for both the histochemical methods and for serum phosphatase determinations.[4]

The preparation of α-naphthylphosphoryl dichloride as described by Kunz[5] was repeated with difficulty and gave poor yields. Good yields were obtained of both alpha and beta isomers by treatment of an equimolar mixture of naphthol and phosphorus oxychloride in dry benzene with one equivalent of pyridine. Di-α-naphthylphosphoryl chloride was similarly prepared from the appropriate amounts of naphthol, phosphorus oxychloride and pyridine.

The hydrolysis of the naphthylphosphoryl dichlorides to the corresponding naphthyl acid phosphates was effected quantitatively by exposure of the acid chlorides to a moist atmosphere over aqueous alkali in an evacuated desiccator. β-Naphthyl acid phosphate was obtained also by solution of the dichloride in water. Kunz[5] reported the preparation of α-naphthyl acid phosphate (m. p. 142°) by hydrolysis of the dichloride with cold water but gave no analysis. The melting point of the product obtained by moist air hydrolysis is twelve degrees higher than that given by Kunz.[5] Hydrolysis of di-α-naphthylphosphoryl chloride to the acid phosphate could not be effected with moist air and was accomplished either with acetone and water or with pyridine and water. With the latter procedure the product was isolated as the pyridinium salt.

Experimental Part[6]

α-Naphthylphosphoryl Dichloride.—A solution of 25 g. of crude α-naphthol and 26.5 g. (15.5 cc.) of phosphorus oxychloride in 90 cc. of dry benzene heated under reflux was treated with 13.7 g. of dry pyridine by slow addition over a period of thirty minutes. During the addition a precipitate of pyridine hydrochloride began to form. The mixture was heated for an additional fifteen minutes, and after cooling, a voluminous precipitate of pyridine hydrochloride was removed by filtration. The solvent was distilled and the residue on distillation gave a fraction, b. p. 195–205°, 70 mm., which on redistillation was obtained as a clear colorless sirup, b. p. 199–201°, 20 mm., $n^{27}D$ 1.596, 34 g. (93%).

α-Naphthyl Acid Phosphate.—When a sample of α-naphthylphosphoryl dichloride as a thin layer (2–3 mm.) was stored in a shallow dish in a partially evacuated desiccator for two days over aqueous potassium hydroxide there occurred a quantitative conversion to α-naphthyl acid phosphate obtained as a white crystalline solid, m. p. 155–157°.

Anal. Calcd. for $C_{10}H_9PO_4$: C, 53.56; H, 4.05. Found: C, 53.72; H, 3.96.

A convenient method for carrying out this transformation in amounts up to 150 g. was provided by the use of large Petri dishes stacked in a vacuum desiccator. Longer periods of five to six days were required for completion of the reaction. The *monosodium salt* was precipitated from a solution of the acid phosphate in methanol by addition of an equivalent of sodium methoxide in methanol.

Di-α-naphthylphosphoryl Chloride.—To a solution of 23.2 g. of crude α-naphthol in 80 cc. of refluxing dry benzene was added at once 7.2 cc. of phosphorus oxychloride and then over a period of thirty minutes a solution of 12.8 cc. of dry pyridine in 20 cc. of dry benzene was added. A precipitate of pyridine hydrochloride formed part way through the addition. Heating was continued for an additional hour. After the mixture cooled, the pyridine hydrochloride was separated on a filter, the solvent was distilled and the residue fractionated at reduced pressure. After separation of the sublimate in the fore-run the fraction, b. p. 250–265°, 0.3 mm., was obtained as a yellow sirup which immediately began to crystallize, 12.5 g. (41%). The product crystallized from benzene-benzin as fine needles, m. p. 88–90°.

Anal. Calcd. for $C_{20}H_{14}PO_3Cl$: C, 65.13; H, 3.83. Found: C, 64.50; H, 3.93.

Di-α-naphthylphosphate. (a) From Di-α-naphthylphosphoryl Chloride in Acetone with Water.—A solution of 1.0 g. of the dichloride in 10 cc. of acetone to which 5 cc. of water was added, was heated on the steam-cone until precipitation of an oil occurred. The oil crystallized after standing for several hours and was obtained as a fine white powder, m. p. 134–137°, 0.9 g. (94%). The product was recrystallized from methanol-water as fine needles, m. p. 137–139°.

Anal. Calcd. for $C_{20}H_{15}PO_4$: C, 68.65; H, 4.28. Found: C, 68.75; H, 4.46.

(b) **In Pyridine with Water.**—A solution of 0.5 g. of di-α-naphthylphosphoryl chloride in two cc. of warm pyridine diluted with 10 cc. of water was heated on the steam-bath for ten minutes and then further diluted to a volume of 50 cc. After standing in the cold the resulting milky suspension precipitated fine shining white flakes. The product which proved to be a pyridinium salt was filtered and after treatment with Norit in hot benzene crystallized as fine fluffy white needles, 0.4 g. (89%), m. p. 105–106°. This material gave a strong odor of pyridine when treated with aqueous alkali.

Anal. Calcd. for $C_{20}H_{15}PO_4 \cdot C_5H_5N$: C, 69.92; H, 4.69. Found: C, 70.47; H, 5.17.

β-Naphthylphosphoryl Dichloride.—The procedure followed was identical to that described for the preparation of α-naphthylphosphoryl dichloride. There was obtained 31 g. of crude product b. p. 145–155°, 1 mm., which on redistillation gave 27 g. (75%) of a water-white sirup b. p. 150–155°, 1 mm. The product crystallized on standing as a solid mass, m. p. 34–35°.

Anal. Calcd. for $C_{10}H_7PO_2Cl_2$: C, 45.97; H, 2.68. Found: C, 45.91; H, 2.61.

β-Naphthyl Acid Phosphate.—A quantitative hydrolysis of β-naphthylphosphoryl dichloride was accomplished in identical manner to that described for the alpha isomer; the product m. p. 176–177°. The identical product was obtained when 2.6 g. of the phosphoryl dichloride was dissolved by warming in 10 cc. of water. On cooling there precipitated 2.0 g. (83%) of granular product, m. p. 176–177°.

Anal. Calcd. for $C_{10}H_9PO_4$: C, 53.56; H, 4.05. Found: C, 53.36; H, 4.24.

The monosodium salt was precipitated from a solution of the acid phosphate in methanol by addition of an equivalent of sodium methoxide in methanol.

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(5) Kunz, *Ber.*, **27**, 2559 (1894).

(6) Analyses by Shirley R. Golden all melting points corrected.

Dehydration Products of α- and β-Amyrin

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α- and β-amyrin are triterpene alcohols having the empirical formula $C_{30}H_{50}O$. Three different

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dehydration products have been reported from each alcohol. In view of the fact that methyl acetylechinocystate has been dehydrated through the methanesulfonyl derivative under very mild conditions and that the process does not appear to involve rearrangement,[1] it seemed desirable to try this method of dehydration on the amyrins. If no rearrangement took place, the product formed should indicate which of the above dienes are primary products and which are rearranged products.

Mesyl α-amyrin was prepared from α-amyrin and methanesulfonyl chloride in pyridine. It was crystallized from methanol and decomposed at 116–118°.

Anal.[2] Calcd. for $C_{31}H_{52}O_3S$: C, 73.75; H, 10.39. Found: C, 73.97; H, 10.28.

After a solution of mesyl-α-amyrin in methanol containing hydrochloric acid was refluxed, only a glassy solid was isolated which could not be crystallized. When solid mesyl-α-amyrin was heated at 90°, it gradually decomposed, and pure α-amyradiene-III,[3] m. p. 193–194°, was isolated from the products. This compound very likely is a rearranged substance, since the methanesulfonic acid formed on decomposition subjects the product to strongly acid conditions at a fairly high temperature.

To avoid the acid conditions, mesyl-α-amyrin was refluxed in pyridine solution. The product melted at 129–131°; $[\alpha]^{20}D$ +148° in chloroform. It depressed the melting points of both α-amyradiene-I[4,5] and of α-amyradiene-II.[5,6,7] Hence it is a new dehydration product which has been named α-amyradiene-IV. It is transparent to ultraviolet light down to 220 mμ.

Anal. Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 88.45; H, 11.44.

Mesyl-β-amyrin prepared from β-amyrin and methanesulfonyl chloride in pyridine and crystallized from methanol decomposed at 127–128°.

Anal. Calcd. for $C_{31}H_{52}O_3S$: C, 73.75; H, 10.39. Found: C, 73.91; H, 10.21.

When solid mesyl-β-amyrin was heated at 105°, no pure compound could be isolated from the decomposition products. When a solution of mesyl-β-amyrin in pyridine was heated, the product was identical with β-amyradiene-II.[6,7]

It is of interest to compare the dehydration of methyl acetylechinocystate and of the amyrins. The dehydration of methyl acetylechinocystate yields the same product when the mesyl derivative is heated with acid methanol or with pyridine, or when the alcohol is heated with phosphorus pentoxide.[8] β-Amyrin gives the same product by decomposition of the benzoate by heat or of the methanesulfonate by refluxing in pyridine, but a different product under acid conditions. α-Amyrin has given a different product by almost every procedure used. Hence one may conclude that the ease of rearrangement on dehydration is echinocystic acid < β-amyrin < α-amyrin.

Which, if any, of the four α-amyradienes is a primary product is difficult to say. α-Amyradiene-II seems to be the most likely candidate since it is obtained both by the decomposition of the benzoate[6] and by the Tschugaev reaction.[7]

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Heat of Combustion and Formation of 1,3,5,7-Cycloöctatetraene and its Heat of Isomerization to Styrene

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In 1947, the authors[1] reported the results of measurements of the heat of combustion of 1,3,5,7-cycloöctatetraene. At that time, the quantity of material available for the investigation was very limited, being only 15 g., and it was not possible to purify the material further nor to evaluate its purity. Recently, Scott, Gross, Oliver and Huffman[2] reported the results of measurements at low temperatures on a sample of cycloöctatetraene of high purity, 99.92 mole per cent. and gave a value for the freezing point for zero impurity and for the cryoscopic constant. From these data and the value of the freezing point of the previous sample, it is calculated that the latter contained about 5.3 mole per cent. of impurity, most probably the isomer, styrene, to which cycloöctatetraene readily isomerizes. Such an amount of impurity, if styrene, would cause the previously reported value[1] for the heat of combustion to be too low by 0.18%. In view of this fact, a sample of the same cycloöctatetraene of high purity measured by Huffman and coworkers[2] was obtained[3] for a redetermination of the heat of combustion. Measurements on the purer sample were made in the same manner as previously reported, with the following result for the heat of combustion, as the mean value from five experiments

C_8H_8(liquid, cycloöctatetraene) + $10O_2$(gas) = $8CO_2$(gas) + $4H_2O$(liquid); $\Delta Hc°_{298.16}$ = −4545.92 ± 0.90 kj./mole, or −1086.50 ± 0.22 kcal./mole

The ± value given in the foregoing, as well as that previously reported for the heat of combustion,

* Editorial Board 1947–.

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(3) From the General Aniline and Film Company, New York, N. Y., through the courtesy of Dr. P. G. Stevens.