the failure of *o*-biphenylylphosphonic acid to undergo cyclodehydration has been previously noted.[6]

We finally succeeded in preparing a derivative of phenoxphosphinic acid by heating *p*-tolyl ether with phosphorus trichloride in the presence of aluminum chloride, and then hydrolyzing the reaction mixture. Since the 4-positions of *p*-tolyl ether are blocked, the phosphorus trichloride attacked the 2-position.[7] The 10-chlorophenoxphosphine which was undoubtedly formed as an intermediate was presumably oxidized during the Friedel-Crafts reaction and subsequently hydrolyzed to 2,8-dimethylphenoxphosphinic acid. No attempt has yet been made to isolate these intermediate chloro compounds.

2,8-Dimethylphenoxphosphinic acid was characterized by analysis and ultraviolet absorption. The spectra of phenoxarsinic and 2,8-dimethylphenoxphosphinic acids are remarkably similar. The slight bathochromic shift exhibited by the phosphinic acid can probably be attributed to the methyl groups [phenoxarsinic acid: λ_{max} (95% ethanol) 214.5 (ϵ 34,400), 240.5 (ϵ 12,700), 275 (ϵ 3,560), 294 (ϵ 5260); 2,8-dimethylphenoxphosphinic acid: λ_{max} 218 (ϵ 35,700), 246 (ϵ 19,300), 297 (ϵ 5,000), 304 mμ (ϵ 5,630).]

In a typical experiment, 9.9 g. of *p*-tolyl ether, 17.4 ml. of phosphorus trichloride, and 8.5 g. of anhydrous aluminum chloride were placed in a 2-necked flask equipped with a sealed stirrer and a reflux condenser protected with a drying tube. The mixture was stirred and refluxed for about 22 hr. On pouring the reaction mixture over 400 g. of cracked ice, an oil was obtained which solidified rapidly. The solid was removed by filtration and washed thoroughly with water. After reprecipitation from 5% sodium hydroxide solution, the solid was recrystallized from 95% ethanol to give a 73% yield of pure 2,8-dimethylphenoxphosphinic acid; m.p. >300°. *Anal.* Calcd. for $C_{14}H_{13}O_3P$: P, 11.90; neut. equiv., 260.2. Found: P, 11.76; neut. equiv., 259.2.

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Received October 19, 1960

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Auto-Transformation of D-Fructose

Sir:

The structural lability of fructose and the variability of its derivatives are well known. We have described a great number of compounds, which are formed by nitrating fructose by different methods and arise from anhydridization, polymerization or degradation.[1–3]

A striking demonstration of the extreme ease with which chemical changes occur in the fructose molecule, even when treated under very mild conditions, is given by treating the sugar with ethanol.

Ten grams of analytically pure, dried D-fructose (the purity of the material was checked chromatographically) was suspended in 10 ml. of absolute ethanol and dissolved by gentle heating to a temperature not exceeding 76°. The solution was kept at this temperature for 12 hr. under careful avoidance of superheating on the walls of the vessel. After cooling, the clear colorless solution was subjected to paper chromatography to yield a spectrum of at least eight spots besides the original spot of fructose. Of these, four had higher and four smaller Rf-values than fructose. By comparing them chromatographically with reference-substances, we were able to identify seven of these spots: methyl glyoxal[1]; difructose anhydride III[4]; methylglyoxal fructoside[1]; difructose anhydride I[4]; diheterolevulosan II[4–5]; diheterolevulosan I[4], β-ethyl fructupyranoside—the latter has also been isolated in substance.

The same results could be obtained in shorter time (in about 2–3 hr.) by boiling fructose with 95% ethanol, which caused immediate solution. The chromatogram in this case was identical with the former one.

A third method for effecting transformations of fructose even without heating, was to keep finely powdered, dried fructose with absolute ethanol at room temperature for some months. Eventually, complete solution occurred and the solution yielded a chromatogram which had besides the eight spots obtained by the first two methods, two additional spots which seemed to represent glucose derivatives.

It follows that under all these conditions, which exclude the action of bases or acids and avoid high temperatures, fructose undergoes anhydridization, dimerization, isomerization and degradation to C_3-fragments.

None of these effects could be observed in aqueous solution of fructose. Alcoholic solutions of glucose also failed to show any change under the conditions of our experiments.

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Received August 2, 1960

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