iodo ketone purified by a vacuum steam distillation at room temperature. Monoiodopinacolone, obtained as a salmon colored oily liquid, is denser than water. Taken up in petroleum ether, it imparted a violet color to the solution, presumably as a result of incipient decomposition.

A sample of the iodinated ketone was divided into four equal portions which were dissolved in equal volumes of methyl alcohol. Some of these tubes were kept in the dark, others in the light. After twenty-four hours the tube contents showed marked increase in color depth. Those kept in the light were affected to a greater extent. In each tube the color was deepest at the top. No appreciable evaporation had occurred; hence, light and especially air, *i. e.*, oxygen, cause the compound to decompose.

Diiodopinacolone.—Attempts to isolate diiodopinacolone were uniformly unsuccessful. When dibromopinacolone was mixed with an aqueous solution of potassium iodide the mixture promptly became orange, indicating synthesis and immediate decomposition.

Conclusions

1. Mono-, di- and tri-chloro-, mono-, di- and tri-bromo-, and mono-iodo-pinacolones have been prepared.
2. The mono-, and tri-chloro-compounds and the mono-iodo ketone are new.
3. By an improved method monobromopinacolone has been produced in good yields. A new method has been devised for the preparation of dibromopinacolone. The tribromo compound has been prepared by a new, and direct, method.
4. Attempts to isolate pure mono- and pure di-iodopinacolone were not successful. These substances seem to be unusually sensitive to light and to air.

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A New Method for the Preparation of the Free Acids and the Abnormal Lactones of the Monobasic Sugar Acids

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The general procedure for the preparation of hexonic acids and in certain cases the corresponding δ-lactones has been by precipitation of the metallic radical of the salts, generally the calcium salt, evaporation of the aqueous solution *in vacuo* from a water-bath heated to 40–50° and extraction of the product with some suitable solvent for recrystallization.

Kiliani[1] prepared the first crystalline hexonic acid and assigned to it the empirical formula ($C_6H_{12}O_7$). He believed this acid to be monomolecular galactonic acid. Later Nef[2] and Hedenburg[3] made a study of this substance and showed that in the crystalline state the acid has instead the

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[1] Kiliani, *Ber.*, **18**, 1551 (1885).

[2] Nef, *Ann.*, **403**, 277 (1914).

[3] Hedenburg, THIS JOURNAL, **37**, 364 (1915).

empirical formula ($C_{12}H_{26}O_{15}$) and is ortho-bis-galactonic acid. Hedenburg and Cretcher[4] prepared a similar *d*-talonic acid having the empirical formula ($C_{12}H_{26}O_{15}$). Rehorst[5] prepared gluconic acid and arabonic acid.

Nef[6] and Hedenburg[7] prepared *d*-gluconic δ-lactone and *d*-mannonic δ-lactone, and Jackson and Hudson[8] prepared *l*-rhamnonic δ-lactone.

Recently Levene and Simms[9] have shown that free acids and δ-lactones in aqueous solution are readily converted to normal lactones. As a consequence the authors have attempted to prepare the acids and their δ-lactones by avoiding the use of water.

The sirupy sodium salts of the acids, prepared by boiling the γ-lactones with sodium bicarbonate solution and evaporation until water free in the case of sodium galactonate, but not necessarily water free in the other cases, were treated with glacial acetic acid. By this procedure crystalline compounds are obtained in good yields, and the sodium acetate formed remains in solution. Following this method, monomolecular *d*-galactonic acid, *l*-rhamnohexonic acid and monomolecular *d*-talonic acid, compounds not hitherto described in the literature, have been prepared and in addition free gluconic acid, *l*-arabonic acid and the δ-lactones of *d*-gluconic, *l*-rhamnonic, and *d*-mannonic acids. The compounds prepared by this procedure appear to be nearly as pure as the recrystallized products.

Galactonic Acid and Ortho-bis-galactonic Acid.—Sodium galactonate obtained as a dry sirup was treated with ten times its weight of glacial acetic acid, warmed until homogeneous, and then chilled. A heavy precipitate of crystals consisting of flat rectangular plates appeared at once. They have a melting point of 145–146°. The compound titrated to its end-point immediately without heating: 0.7964 g. required 40.89 cc. of 0.1 N NaOH; calcd. for ($C_6H_{12}O_7$), 40.61 cc. of 0.1 N NaOH; $[\alpha]^{25}_{D}$ $-13.09°$ (three minutes). Analysis for water evolved at the melting point gave 0.0564 g. of water for 0.6258 g. of the free acid, equivalent to 9.01%; calcd. 9.18% for conversion of the acid to the lactone. Recrystallization of the above monomolecular acid from a water–alcohol solution gave Hedenburg's ortho-bis-galactonic acid, m. p. 141–142°. Analysis for water evolved at the melting point gave 12.87%; calcd. 13.17% for conversion of the ortho-bis-galactonic acid to the lactone.

1-Rhamnohexonic Acid.—The sirupy sodium salt containing some water was treated with ten times its weight of glacial acetic acid and the solution chilled in ice water. A copious crystalline precipitate formed. Recrystallization was accomplished by dissolving in the smallest amount of water and precipitating by the addition of alcohol; melting point, 174–175°; $[\alpha]^{25}_{D}$ $+19.15°$ (ten minutes); $+17.14°$ (one hour and thirty minutes); and $+60.3°$ (twelve days). It titrated instantly and completely without heating: 0.2674 g. required 12.58 cc. of 0.1 N NaOH; calcd. for ($C_7H_{14}O_7$), 12.73 cc. of 0.1 N NaOH.

***d*-Talonic Acid.**—The sirupy sodium salt containing some water was treated with ten times its weight of glacial acetic acid and the solution chilled in ice water. A

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[4] Hedenburg and Cretcher, THIS JOURNAL, **49**, 478 (1927).

[5] Rehorst, *Ber.*, **61**, 163 (1928); **63**, 2279 (1930).

[6] Nef, *Ann.*, **403**, 306 (1914).

[7] Hedenburg, THIS JOURNAL, **37**, 345 (1915).

[8] Jackson and Hudson, *ibid.*, **52**, 1270 (1930).

[9] Levene and Simms, *J. Biol. Chem.*, **65**, 31 (1925).

copious precipitate was formed. Recrystallization was accomplished by dissolving in the smallest amount of cold water necessary for solution and precipitating by the addition of acetic acid. The melting point of the substance before and after recrystallization was found to be the same; melting point 138–139°, $[\alpha]_D^{25}$ +18.71° (five minutes). Analysis for water evolved at the melting point gave 0.0646 g. of water for 0.6836 g. of the free acid, equivalent to 9.45%; calcd. 9.18% for conversion of the acid to the lactone.

***d*-Gluconic Acid.**—A nearly quantitative yield of free gluconic acid was obtained in a manner analogous to that used for rhamnohexonic acid. The product had a melting point of 125–126° after recrystallization from water by the addition of acetic acid; $[\alpha]_D^{25}$ −4.75° (five minutes). Rehorst[5] found m. p. 125–126°, $[\alpha]_D^{20}$ −6.72° (five minutes).

***l*-Arabonic Acid.**—Sodium arabonate was prepared from the calcium salt without isolating the lactone. Treatment of the sodium salt in a manner analogous to that used for rhamnohexonic acid gave a 70% yield of free arabonic acid. The product had a melting point of 111–115° after recrystallization from cold water by the addition of acetic acid, $[\alpha]_D^{25}$ −8.73° (five minutes). Rehorst[10] found that the compound softens at 110–111° and melts at 118–119°, and $[\alpha]_D^{20}$ −9.55° (five minutes).

***d*-Gluconic δ-Lactone.**—Sodium gluconate was warmed with glacial acetic acid to 60° and the solution allowed to cool. Addition of a crystal of the δ-lactone caused the lactone to crystallize out, m. p. 146°, $[\alpha]_D^{25}$ +66.74° (three minutes) and +8.51° (four hours and twenty minutes). Nef[6] found m. p. 145–150°; recryst. 150–152°, $[\alpha]_D^{20}$ +61.7° (twelve minutes), +10.0° (two hours and thirty minutes).

***l*-Rhamnonic δ-Lactone.**—Sodium rhamnonate was warmed with glacial acetic acid and allowed to cool. On stirring the solution a heavy precipitate of the δ-lactone formed. The compound had a melting point of 172–177°, $[\alpha]_D^{25}$ −97.9° (five minutes). Jackson and Hudson[8] found m. p. 172–181°, $[\alpha]_D^{23}$ −98.4° (seven minutes).

***d*-Mannonic δ-Lactone.**—Sodium mannonate yielded crystals of the δ-lactone when treated with glacial acetic acid at 25° and allowed to stand for several days. The original product had a melting point of 160–161°, $[\alpha]_D^{25}$ +112.7° (six minutes). Hedenburg[7] found m. p. 161–162°, $[\alpha]_D^{20}$ +111.85° (six minutes).

Summary

1. A new method has been developed for the preparation of free acids and δ-lactones.
2. Three new compounds, monomolecular *d*-galactonic acid, *l*-rhamnohexonic acid and *d*-talonic acid have been prepared by this method.
3. The method has been applied successfully to the preparation of *d*-gluconic acid, *l*-arabonic acid, *d*-gluconic δ-lactone, *l*-rhamnonic δ-lactone, and *d*-mannonic δ-lactone.

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[10] Rehorst, *Ber.*, **63**, 2279 (1930).