

Anal. Calcd. for $C_{22}H_{21}O_2Br$: C, 66.49; H, 5.33. Found: C, 66.46, 66.67; H, 4.76, 4.66.

The second compound, a bromo-1,6-dimethyldihydropleiadene, was best prepared as follows: 1 g. of the primary bromination product was shaken in the cold with 4 cc. of pyridine for one-half hour. The needles gradually disappeared and when dissolution was nearly complete a colorless powder began to separate. Enough alcohol was added to bring this material into solution at the boiling point and the solution was set aside to crystallize. The bromo compound separated in a very pure condition in the form of long, slender needles (0.8 g.). The substance distills without decomposition and may be recovered unchanged after prolonged boiling with alcoholic alkali. No coloration is produced with cold concd. sulfuric acid, but on heating the solution acquires an intense red color. The melting point is 179°.

Anal. Calcd. for $C_{20}H_{17}Br$: C, 71.21; H, 5.08. Found: C, 71.22; H, 5.15.

Summary

In extending earlier investigations various new pleiadenediones, pleiadones and dihydropleiadenes have been prepared and characterized.

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Preparation of *l*-Tartaric Acid by the Oxidation of *d*-Gulonic Lactone

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Fischer and Crossley¹ obtained a 5% yield of potassium acid *d*-tartrate by the oxidation of potassium acid *d*-saccharate with alkaline permanganate. In a patented process Odell² claimed a substantial yield of *d*-tartaric acid together with *d*-saccharic acid by the oxidation of *d*-glucose with nitric acid in which was dissolved a small amount of sodium vanadate. It seemed probable that the formation of *d*-tartaric acid in the Odell process might be due, at least in part, to a secondary oxidation of the saccharic acid formed in the early stages of the reaction. This view was substantiated by the fact that the authors obtained *d*-tartaric acid in appreciable yields from both *d*-gulonic and *d*-saccharic lactones by their oxidation with nitric acid containing a trace of a vanadate.

Since *d*-gulonic lactone gives *l*-saccharic³ acid on oxidation with nitric acid alone, it should give *l*-tartaric acid in addition when oxidized with nitric acid containing a trace of the vanadate catalyst. Moreover the process involves no difficulties and, thanks to the researches⁴ that have taken xylose out of the category of rare sugars, *d*-gulonic lactone may be readily obtained.

(1) Fischer and Crossley, *Ber.*, **27**, 394 (1894).

(2) Odell, U. S. Patent 1,425,605.

(3) Fischer, *Ber.*, **23**, 2611 (1890); Fischer and Stahel, *ibid.*, **24**, 534 (1891).

(4) Hudson and Harding, *This Journal*, **40**, 1601-1602 (1918); Monroe, *ibid.*, **41**, 1002-1003 (1919); Schreiber, Geib, Wingfield and Acree, *Ind. Eng. Chem.*, **32**, 497-501 (1930).

Experimental

d-Gulonic lactone was prepared from xylose by the method of LaForge,⁵ with about the same results and yield as obtained by him. Fifty grams of this lactone was dissolved in 25 cc. of water and 105 cc. of concentrated nitric acid containing 0.01 g. of sodium metavanadate. The solution was warmed on a water-bath for a few minutes, but removed when a reaction became noticeable. This oxidation is exothermic and became very vigorous within a few minutes, a copious cloud of nitrogen dioxide being evolved. After the reaction had subsided, the solution was evaporated on a boiling bath until judging by the odor all nitrogen dioxide and volatile acids had been expelled. The somewhat sirupy product was chilled in an ice-bath and oxalic acid dihydrate amounting to 13.6 g. (after drying in air) was removed by filtration. The filtrate diluted to about 100 cc. was one-half neutralized with a 60% potassium hydroxide solution. Within a few minutes crystallization of a mixture of potassium acid *l*-saccharate and potassium acid *l*-tartrate commenced and was complete on standing overnight at room temperature. The crystals were filtered off, washed with a little cold water, then with 60% alcohol. After drying the weight was 22.3 g. One gram required 22.7 cc. of *N*/5 alkali for neutralization. A sample neutralized with potassium hydroxide showed $[\alpha]_D^{20} = -12.4$ calculated on the neutral potassium tartrate in the polarized solution. These figures showed the composition of the mixed potassium acid salts to be approximately 39% potassium acid *l*-tartrate and 61% potassium acid *l*-saccharate.

A separation of these salts was effected to a large extent by taking advantage of the far greater solubility of the acid saccharate in boiling water; 21.3 g. of the mixed salts was boiled with 66 cc. of water under a reflux condenser for one-half hour. The undissolved fraction was filtered off, washed with a little water and dried. There was obtained 8.6 g. which was now 95% potassium acid *l*-tartrate. This salt was quantitatively converted to *l*-calcium tartrate by neutralizing and adding a slight excess of 25% calcium acetate solution. The small amount of *l*-calcium saccharate formed at the same time remained in solution. The calcium salt was powdered, suspended in water on a boiling water-bath and decomposed with the calculated amount of oxalic acid. After filtering off the precipitated calcium oxalate, the acid filtrate was evaporated to a thin sirup which readily crystallized. The crystals were separated from their mother liquor by filtration with suction and washed with a little ice water. The filtrate was half neutralized with potassium hydroxide yielding a crop of pure potassium acid *l*-tartrate.

The acid crystals dried over sulfuric acid were pure *l*-tartaric acid; 0.5 g. titrated 33.3 cc. of *N*/5 alkali, calcd. 33.33 cc.; 1.0 g. in 25 cc. of solution read -2.27° in a 4-dm. tube, hence $[\alpha]_D^{20} = -14.2$.

The potassium acid salt from the mother liquor was pure potassium acid *l*-tartrate; 0.5 g. titrated 13.25 cc. of *N*/5 alkali, calcd. 13.29; 1.0 g. exactly neutralized with potassium hydroxide showed $[\alpha]_D^{20} = -28.0$, calculated on the basis of the amount of neutral potassium tartrate in the polarized sample.

Calculating the potassium acid salt to tartaric acid and allowing for samples removed for analysis, the yield of *l*-tartaric acid from 50 g. of *d*-gulonic lactone was 6.8 g.

Summary

A yield of 13.6% of *l*-tartaric acid has been obtained by the oxidation of *d*-gulonic lactone, a substance which itself is readily obtained from xylose.

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(5) LaForge, *J. Biol. Chem.*, **36**, 347 (1918).