conjugated with the triple bond is readily and completely iodinated by a solution of iodine in ammonia at its boiling point. For such acetylenes iodination in liquid ammonia offers the best method for the preparation of the iodoacetylene.

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[CONTRIBUTION FROM THE KENT AND JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Resolution of *dl*-Erythronic Acid[1]

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One of the by-products in the preparation of 2,3-dihydroxybutyric acid is a lactone which we have called 3-hydroxyisocrotonic lactone.[2] The yield of this by-product in the process employed is fairly high (about 23%). It has proved possible to convert this lactone with excellent yield into *dl*-erythronic lactone[3] and a good supply of the latter is now on hand. Experiments are being conducted with the object of reducing the erythronic lactone to erythrose and, in order to obtain the active erythroses, it is necessary to have the corresponding active erythronic lactones. The work reported below was carried out for the purpose of supplying these necessary active lactones.

All three varieties of erythronic acid—*dl*, *d* and *l*—are known in the form of their 1,4 lactones.[4,5,6] The resolution of the *dl*-acid has been twice attempted but neither attempt was entirely successful.[7] This paper reports the complete resolution of the *dl*-acid by the use of brucine and quinine and gives the constants of the two pure optically active lactones.

Experimental Part

The *dl*-Erythronic Lactone.—The *dl*-lactone used in this work was prepared in 61% yield according to the method of Braun by the oxidation of 3-hydroxyisocrotonic lactone with silver chlorate. It was recrystallized from ethyl acetate and then melted at 91–92° and was shown, by titration, to be perfectly pure.

The Resolution.—Preliminary experiments showed that either brucine or quinine could be used as the resolving agent. Recrystallization of the brucine salts from water gave the pure brucine salt of the levorotatory component and recrystallization of the quinine salts from 95% alcohol gave the pure dextrorotatory component. The yields of pure lactone obtained when a single alkaloid was used, however, were not good and the two pure lactones were obtained in larger quantities by the alternate use of brucine and quinine. This procedure is made possible by the fact that of the two brucine salts it is the *d*-(–)-form that is the less soluble and of the two quinine salts the *l*-(+)-form that is the less soluble.

The procedure used was to convert the lactone into its brucine or quinine salt by the usual methods. In the case of the brucine salt, the water solution was then concentrated *in vacuo* at 60° until the ratio of water to salt was 2 to 1, cooled, and stored in the ice box for twenty-four to forty-eight hours. The crop of crystals (Crop 1) was removed by suction filtration but not washed. The mother liquor from Crop 1 was concentrated until the ratio of water to salt was again 2 to 1 and a second crop of crystals (Crop 2) obtained. Crops 1 and 2 were now united and recrystallized from 2 parts of water; Crop B1A was thus obtained. The mother liquor from Crop B1A was added to that from Crop 2. The lactone was set free from Crop B1A and found to be fairly pure *d*-(–)-lactone (see table below).

The combined mother liquors were now hydrolyzed and the lactone obtained was converted into the quinine salt. Again two crops of salts were obtained as in the case of the brucine salt except that 5 parts of 95% alcohol were used. The two crops were united and recrystallized from 5 parts of 95% alcohol and thus yielded Crop Q2A. The mother liquor from Crop Q2A was added to the mother liquor from quinine salt Crop 2. The lactone was set free from Crop Q2A and found to be fairly pure *l*-(+)-lactone (see table below).

The lactone was set free from the quinine salts in the combined mother liquors and converted back into the brucine salt and the process outlined above repeated; two crops of brucine salt obtained and recrystallized from two parts of water gave Crop B3A. The mother liquors gave a lactone that was converted into the quinine salt; this yielded two crops which were combined and recrystallized and gave Crop Q4A. This cycle was again repeated and Crops B5A and Q6A obtained. Crops B3A and B5A were now united as were also Crops Q4A and Q6A and the lactones set free.

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(1) The material in this article is taken partly from a dissertation presented by Louis R. Forbrich in partial fulfilment of the requirements for the degree of Master of Science in the University of Chicago.

(2) Glattfeld, Leavell, Spieth and Hutton, THIS JOURNAL, **53**, 3164 (1931).

(3) Braun, *ibid.*, **51**, 235 (1929).

(4) Lamparter, *Ann.*, **134**, 260 (1865); Sell, *Z. Chem.*, **8**, 12 (1865); Neuberg, *Chem. Centr.*, I, 1229 (1910); Nef, *Ann.*, **357**, 247 (1909); Anderson, *Am. Chem. J.*, **42**, 402 (1909); Lespieau, *Bull. soc. chim.*, [iv] 1, 1117 (1907); Cohen, Abstracts of Theses, University of Chicago, Sciences Series, V1, 125 (1927–28); Braun, *loc. cit.*

(5) Ruff, *Ber.*, **32**, 3672 (1899); Glattfeld, *Am. Chem. J.*, **50**, 148 (1913); Jensen and Upson, THIS JOURNAL, **47**, 3021 (1925).

(6) Ruff, *Ber.*, **34**, 1368 (1901).

(7) Lespieau, *loc. cit.*; Anderson, *loc. cit.*

EXPERIMENT 1

100 g. of Lactone and 392 g. of Brucine to Start

Crop B1A, 72 g.	→ lactone, 16 g. (−66.4°)	total *d*-(−)-lactone, 30 g.
Crop B3A, 68 g. Crop B5A, 28 g.	→ lactone, 14 g. (−60.0°)	
Crop Q2A, 92 g.	→ lactone, 22 g. (+70.6°), total *l*-(+)-lactone, 22 g.	
Crop Q4A, 45 g. Crop Q6A, 16 g.	→ lactone, 15 g. (+17.5°), discarded	

EXPERIMENT 2

50 g. of Lactone and 147 g. of Quinine to Start

Crop Q1A, 47 g.	→ lactone, 11 g. (+69.4°)	total *l*-(+)-lactone, 12.87 g.
Crop Q3A, 27 g. Crop Q5A, 11 g.	→ lactone, 1.87 g. (+73.0°)	
Crop B2A, 60 g.	→ lactone, 10.5 g. (−66.59°)	total *d*-(−)-lactone, 14.0 g.
Crop B4A, 25 g. Crop B6A, 7 g.	→ lactone, 2.5 g. (−71.6°)	

The resolution was then repeated, starting with quinine and results similar to those in the first experiment obtained. These are recorded in the table. Rotations in this paper are for sodium light and approximately 4% aqueous solutions unless otherwise indicated.

It is seen that the total recovery of active lactone in the first case is 52% of the theoretical and in the second case 53% of the theoretical. It will be noted that the yield of lactone from the combined second and third crops of both quinine and brucine salts in Experiment 2 is low. This is due to the fact that the crude lactones obtained by the hydrolysis of these salts were of low optical activity and had to be recrystallized repeatedly from ethyl acetate in order to purify them. Thus the 38 g. of quinine salts in Experiment 2 gave 8 g. of lactone [+38°]; this was four times recrystallized and then yielded only 1.87 g. [+73°]; similarly in the other cases where the yield of lactone seems abnormally low. Only crude lactones of specific rotation about 40° or above will yield pure lactones of proper rotation by this process of recrystallization. In Experiment 1 the 15 g. of crude lactone from 61 g. of quinine salts was of such low activity (+17.5) that it was useless to try to obtain pure lactone from it by recrystallization. Unless conservation of material is very important, it is not worth while to attempt to obtain more than two crops of brucine and quinine salts (B1A and B3A; Q2A and Q4A). Subsequent crops do not yield lactones of a very high degree of purity.

The Pure Active Lactones.—From the experiments described above and other similar ones, 51 g. of *l*-(+)-lactone and 60 g. of *d*-(−)-lactone with rotations above 60° were obtained. These two lots of material were four times recrystallized from ethyl acetate. The first crops (31.77 g. and 37.18 g.) had specific rotations of +72.53 and −72.41 and the fourth crops (6 g. and 10 g.) +73.05 and −72.98, respectively. The specific rotations of these pure lactones with mercury light (546) were found to be +87.32 and −87.62, respectively. The lactones melt at 105° (corr.). When allowed to crystallize slowly from ethyl acetate they form long glistening needles.

Summary

dl-Erythronic lactone, prepared by the oxidation of 3-hydroxyisocrotonic lactone, has been resolved completely by the alternate use of brucine and quinine with a recovery of over 50% of material in the form of pure active lactones. The pure *d*-(−) and *l*-(+) lactones obtained had specific rotations (Hg light 546) of −87.6 and +87.3 (Na light) −72.9 and +73.0; melting points (corr.) of 105°.

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