Anal. Calcd. for $C_{20}H_{14}O_2S_3$: C, 62.9; H, 3.67. Found: C, 63.0; H, 3.70.

When a sample of this material, m.p. 148–150°, was mixed with the first crop obtained by the other method, m.p. 149.5–150.5°, the melting point of the mixture was 148.0–149.5°.

Bis-(3-thianaphthacyl) Sulfone.—To a suspension of 2.0 g. of bis-(3-thianaphthacyl) sulfide in 40 cc. of glacial acetic acid held at 70–85° was added over a ten-minute period a solution of 1.8 cc. of 30% hydrogen peroxide in 4 cc. of glacial acetic acid. After ten more minutes an additional 0.2 cc. of hydrogen peroxide in 3 cc. of acetic acid was added. After ten more minutes at 70–85° the mixture was cooled and diluted with water. The precipitate was separated by filtration, washed with water and dried to yield 0.3 g. (14%) of crude bis-(3-thianaphthacyl) sulfone. An analytical sample was crystallized three times from a mixture of toluene and ethanol, m.p. 236–237°.

Anal. Calcd. for $C_{20}H_{14}O_4S_3$: C, 58.0; H, 3.38. Found: C, 58.6; H, 3.70.

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The Synthesis of L-Lyxonic Acid

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D-Lyxonic acid has been reported several times, but L-lyxonic acid apparently has not been synthesized. D-Lyxonic acid has been obtained as a sirup by the oxidation of the readily available D-lyxose[1,2] and also by the epimerization of D-xylonic acid.[3] The application of these two methods for the preparation of L-lyxonic acid is obvious. However, both L-lyxose and L-xylose are not easily obtained starting compounds.

L-Xylonic acid was prepared by the oxidative degradation[4] of 2-keto-L-gulonic acid. The L-xylonic acid was separated as the cadmium bromide double salt[5,6] which was resolved to the L-xylonic acid and characterized as the 1,4-anhydro-L-xylobenzimidazole derivative. L-Xylonolactone was epimerized to L-lyxonic acid which was characterized as its benzimidazole derivative.

L-Lyxose was prepared by a modified Ruff reaction[7] from calcium L-galactonate and was oxidized by iodine[8] in an alkaline methanol solution. This gave L-lyxonic acid which was separated as the barium salt and subsequently freed of barium ion. The L-lyxonic acid was again obtained as an uncrystallized sirup and was identified as the benzimidazole derivative.

Experimental

Cadmium-L-xylonate-cadmium Bromide Dihydrate.[4,5,6]—Fifty grams of 2-keto-L-gulonic acid was treated with 15 g. of sodium carbonate in 300 ml. of water. The solution was cooled, and 32 ml. of 30% hydrogen peroxide dropped in at 0° over a period of 1 hour. Then a slight excess of concd. HCl was added (foaming), and the solution concentrated to a sirup. The sirup was then diluted to 300 ml. and digested with about 25 g. of powdered cadmium carbonate. The excess cadmium carbonate was removed by filtration after complete reaction and 40 g. of cadmium bromide added. On cooling and with the addition of alcohol to turbidity, 23.5 g. of crude complex separated. The complex was purified by solution in 100 ml. of water, decolorized and on cooling separated by crystallization as a colorless, crystalline compound. Concentration of the mother liquor gave a further small yield; $[\alpha]^{26}\mathrm{D}$ −10.5° (c, 1, H_2O). The analogous D-complex has been reported to have rotations of $[\alpha]\mathrm{D}$ +7.4°[9] and $[\alpha]^{20}\mathrm{D}$ +8.8°.[10]

Anal. Calcd. for $Cd(C_5H_9O_6)_2CdBr_2 \cdot 2H_2O$: C, 16.0; H, 2.9; Br, 21.3. Found: C, 15.7; H, 2.9; Br, 21.3.

1,4-Anhydro-L-xylobenzimidazole.—In 500 ml. of hot water 2.5 g. of cadmium-L-xylonate-cadmium bromide dihydrate was dissolved, and hydrogen sulfide was passed in until all of the cadmium had been precipitated. The clarified solution was concentrated to 10 ml. and treated with 1.5 g. of *o*-phenylenediamine as described for the D-isomer.[8] The product was purified by extraction with ice-water five times, using 5 ml. of water for each extraction, to remove soluble salts. The residue was recrystallized from about 10 ml. of water containing ammonia; yield 0.8 g. (50%); m.p. 224–226° (uncor.), $[\alpha]^{28}\mathrm{D}$ −63° (c, 0.6, 5% citric acid).

Anal. Calcd. for $C_{11}H_{12}O_3N_2$: N, 12.7. Found: N, 12.8.

After completion of our work this compound was reported[11] having been synthesized from *o*-phenylenediamine and 2,5-anhydro-L-xylonic acid. The benzimidazole was reported, m.p. 225–228°; $[\alpha]^{25}\mathrm{D}$ −64.6° (5% citric acid soln.).

The corresponding D-compound[8,12] has a m.p. 224°; $[\alpha]^{25}\mathrm{D}$ +64.8° (5% citric acid soln.).

L-Lyxonic Acid from L-Xylonic Acid.[3]—Cadmium-L-xylonate-cadmium bromide dihydrate (20 g.) was dissolved in 300 ml. of water and 55 ml. of 1 *N* HCl acid was added. To this solution was added 1200 ml. of pyridine, and the solution was heated in an autoclave under nitrogen (500 lb.) at 140–145° for 3.5 hours. The pyridine was removed by distillation, and then the residue dissolved in 200 ml. of water and digested with 10 g. of cadmium carbonate. The excess cadmium carbonate was removed by filtration, and the solution concentrated to 50 ml. On cooling, 5.35 g. of the unepimerized cadmium xylonate complex separated. Further concentration gave only traces of the complex salt. The viscous solution was diluted to 500 ml., the cadmium removed by hydrogen sulfide, and the halides by silver oxide. Concentration to a sirup and dehydration using ethanol gave 4.4 g. of crude sirup (60%). This material did not crystallize.

2-(L-Lyxotetrahydroxybutyl)-benzimidazole.—Crude L-lyxonic acid sirup (2 g.) was treated with *o*-phenylenediamine according to Link's procedure[8] for D-lyxonic acid. The recovered product was purified as described above for the xylo derivative; yield 0.7 g. (24%); m.p. 188–189°; $[\alpha]^{25}\mathrm{D}$ +11.3° (c, 1, 5% citric acid soln.).

Anal. Calcd. for $C_{11}H_{14}O_4N_2$: N, 11.8. Found: N, 11.5.

The corresponding D-form has been reported[8]: m.p. 189°; $[\alpha]^{25}\mathrm{D}$ −12.8°.

L-Lyxonic Acid from L-Lyxose.—L-Lyxose (4 g.) was obtained as a sirup from calcium-L-galactonate by a modified Ruff procedure,[7] and was converted into the barium salt in the manner described for D-lyxonic acid[8]; yield 3.7 g. This amorphous salt was dissolved in 100 ml. of hot water and the barium precipitated by the addition of a solution of 1.3 g. of oxalic acid hydrate in 10 ml. of water. After filtration, the excess oxalic acid was removed by silver oxide, and the L-lyxonic acid liberated by hydrogen sulfide. The solution of L-lyxonic acid was concentrated to a sirup which could not be induced to crystallize. The benzimidazole derivative was prepared as described above; m.p. 188–189°; $[\alpha]^{25}\mathrm{D}$ +11.0°; mixed m.p. with 2-(L-lyxotetrahydroxybutyl)-benzimidazole prepared from L-lyxonic acid obtained by epimerizing L-xylonic acid; m.p. 187–188°. This confirms the generality of both methods for the preparation of L-lyxonic acid.

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