then added slowly, and the resulting mixture was refluxed for one hour. After cooling to room temperature the fine precipitate was filtered off: 1.00 g. of white powder, m.p. 185–187° dec. A second crop was obtained by concentrating the filtrate to 40 ml.: 0.36 g., m.p. 185–187° dec. These were combined and stirred with 150 ml. of $^2/_3$% aqueous potassium hydroxide whereupon complete solution followed by precipitation of brucine occurred. The brucine was filtered off and the filtrate was acidified carefully with concd. hydrochloric acid (3 ml.). The resulting oily precipitate was digested at 0° until it crystallized and then it was recrystallized from chlorobenzene to give a product which appeared to decompose above 130°, resolidify and melt with decomposition at 211–212°, $[\alpha]^{28}\mathrm{D}$ −28.7° (absolute ethanol, *l* 1 dm., *c* 4.61 g./100 ml.).

Anal. Calcd. for $C_{19}H_{16}O_5 \cdot H_2O$: C, 66.66; H. 5.30. Found (S): C. 66.31, 66.27; H, 5.10, 5.14.

Resolution of 2-*exo*-Hydroxy-3,4,7,8-dibenzo[3.2.1]bicyclooctadiene-*cis*-6-dicarboxylic Acid-2,6-lactone (IIa).—The lactone-acid (IIa,[4] 3.51 g., 0.0115 mole) was dissolved in 20 ml. of hot absolute ethanol and added to 3.72 g. (0.0115 mole) of quinine in a like volume of the same solvent. Cooling the mixture in an ice–salt-bath caused the separation of 4.52 g. of salt, m.p. 207.5–210.5° dec. This was recrystallized four times from absolute ethanol until a constant melting point and rotation were obtained. The recrystallizations were conducted by dissolving the salt in excess solvent then evaporating the solution in a current of air to the point of incipient turbidity on the steam-bath. Enough alcohol then was added to dissolve the solid completely, and the solution was allowed to cool to room temperature, then further cooled in an ice–salt-bath.

The final product (m.p. 221.0–222.0° dec., $[\alpha]^{28}\mathrm{D}$ −209°, dimethylformamide, *l* 1 dm., *c* 5.55 g./100 ml.) was triturated with 15 ml. of 10% hydrochloric acid causing separation of a gum which became crystalline after several minutes scratching with a glass rod. The resulting solid was filtered off and recrystallized from acetic acid–water as the monohydrate of (−)-IIa (fine white prisms); the yield was 0.283 g. (15%). The rotation of the material was taken in absolute ethanol and showed $[\alpha]^{28}\mathrm{D}$ −253° (*l* 1 dm., *c* 6.25 g./100 ml.).

When heated in a capillary tube, the material sintered to form a translucent bead on the wall at 116–118°. As the temperature was raised slowly, gas began to evolve. The evolution was complete at 145° by which time the bead had gradually fallen into a transparent glass at the bottom of the tube. It remained in this state when removed from the bath and allowed to cool, so remelting behavior could not be observed.

Anal. Calcd. for $C_{19}H_{14}O_4 \cdot H_2O$: C, 70.36; H, 4.98. Found (S): C, 70.33, 70.27; H, 5.08, 5.11.

Reaction of (−)-2-Hydroxy-3-methyldibenzo[2.2.2]bicyclooctadiene-*trans*-2,3-dicarboxylic Acid with 48% Hydrobromic Acid.[4]—In 75 ml. of 48% hydrobromic acid, 0.561 g. (0.00173 mole) of (−)-Ia ($[\alpha]^{28}\mathrm{D}$ −28.7°) was dissolved by warming on the steam-bath. Solution was complete after a few hours and the mixture was heated for a total of 24 hours. The solution was then evaporated on a hot-plate to *ca.* half its original volume by an air stream. One recrystallization from acetic acid–water with the aid of Norit left 0.387 g. (69%) of the monohydrate of rather indefinite melting point. Three successive recrystallizations from acetic acid–water resulted in fine white prisms which exhibited melting behavior similar to the (−)-form described above.

A mixed melting point determination with roughly an equivalent amount of the (−)-form showed softening beginning at 112°, but the melt resolidified by the time the temperature reached 130°. It then melted with decomposition at 224.0–227.5°. When a mixture containing roughly three parts of the (+)-form to one part of the (−)-form was heated in a capillary tube the melting behavior was very similar to the pure (+)-form except that at 170° formation of a few crystals on the side of the capillary began. These began to soften around 190° and continued to soften gradually until by 230° the whole had been transformed into a transparent glass.

The infrared spectrum of this material was identical with that of its enantiomer obtained by resolution, and both optically active forms showed an absorption at 3440 cm.$^{-1}$ which was lacking in the anhydrous racemic compound.

The optical rotation was observed in absolute ethanol and found to be $[\alpha]^{23}\mathrm{D}$ +256° (*l* 1 dm., *c* 7.95 g./100 ml.).

Anal. Calcd. for $C_{19}H_{14}O_4 \cdot H_2O$: C, 70.36; H, 4.98. Found (S): C, 70.54, 70.54; H, 5.52, 5.52.

The methyl ester was prepared (diazomethane) and recrystallized from methanol–water. It became crystalline only after standing three days in the refrigerator. The melting point was indefinite, the material never became liquid; only a transparent glass was formed slowly, beginning at about 75°. Recrystallization from methanol–water and drying over phosphorus pentoxide 48 hours at 56° (0.05 mm.) failed to alter the melting behavior. The infrared spectrum of this material was identical with the spectrum of the methyl ester of racemic IIa.[4]

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: (S): C, 74.90; H, 4.98.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Crystalline 4-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-D-arabo-3-hexulose. A New Route to Talitol Derivatives

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Monobenzoylation of 1,2:5,6-di-*O*-isopropylidene-D-mannitol followed by oxidation with chromic acid–pyridine gave crystalline 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose. Lithium aluminum hydride reduction of the latter yielded 1,2:5,6-di-*O*-isopropylidene-D-talitol and -D-mannitol. The application of a cation-exchange resin to catalyze the hydrolysis of isopropylidene groups is described.

Although aldohexoses and 2-hexuloses have been studied extensively, the 3-hexuloses have received but limited attention. Recently, the preparation of sirupy 2-*O*-methyl-L-*xylo*-3-hexulose, characterized as its crystalline 2,5-dichlorophenylhydrazone, was described.[1] The direct conversion of the methyl ether to the parent sugar does not appear to be feasible. In this investigation an approach was planned which to us appeared to offer more possibilities in realizing the synthesis of an unsubstituted 3-hexulose.

1,2:5,6-Di-*O*-isopropylidene-D-mannitol was used as the starting compound. The elegant synthesis[2] described for this substance made this choice attractive. Benzoylation with an equimolar amount of benzoyl chloride gave the crystalline 3-*O*-benzoate (46%). The equivalence of the two open positions precludes any isomeric product.

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The oxidation of 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol to a substituted ketose was realized using the complex formed by the reaction of chromic acid and pyridine.[3] This oxidizing system has been described[3] as applicable to primary and secondary alcohols, containing acid-sensitive groups, in preparing aldehydes and ketones. The polyol derivative used in this study contained not only the acid-sensitive isopropylidene groups but also the acid- and base-sensitive benzoate ester groups. However, yields of crystalline 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose as high as 50% were obtained. Thus this oxidizing agent appears to have considerable promise in its application to the oxidation of carbohydrate derivatives.

The reduction of 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose with lithium aluminum hydride gave the expected products, 1,2:5,6-di-*O*-isopropylidene-D-mannitol and 1,2:5,6-di-*O*-isopropylidene-D-talitol, confirming the structure assignment of the parent ketose. A combination of fractional crystallization and column chromatography permitted an excellent separation of the two compounds, recovered in a combined amount of 94% in crystalline form. The molar ratio of the mannitol derivative to the talitol derivative was 1.17 to 1. The stereospecificity exhibited in lithium aluminum hydride reduction reactions has been studied extensively.[4] The 3-hexulose derivative has the carbonyl group flanked by two asymmetric carbon atoms. Moreover, the presence of the several electronegative oxygen atoms adds another complication. Thus we are unable to provide any logical explanation for the predominance of the one isomer over the other.

The crystalline 1,2:5,6-di-*O*-isopropylidene-D-talitol was hydrolyzed readily to D-talitol, from which the known tribenzylidene derivative was prepared. The hexaacetate was obtained only as a sirup. The di-*O*-isopropylidene derivative should serve as a useful starting compound for the synthesis of other partially substituted and mixed derivatives of D-talitol.

Preliminary studies on 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose demonstrated the marked acid-lability of this compound. Prompted by the need for a gentle method for the hydrolysis of ketal groups, the possibility of using a cation-exchange resin was considered. Cation-exchange resins have been applied in the formation and hydrolysis of esters,[5] in the preparation of isopropylidene derivatives of carbohydrates,[6,7] in the hydrolysis of a 6-*O*-methyl-di-*O*-methylene-D-glucose[6] and in the formation of glycosides.[6,7] The hydrolysis of 1,2:5,6-di-*O*-isopropylidene-D-mannitol and of 1,2:5,6-di-*O*-isopropylidene-D-talitol occurred smoothly in aqueous acetone using Amberlite IR-120.[8] With the mannitol derivative, the yield of the polyol was essentially quantitative. The application of the same procedure to 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol gave a monobenzoate of D-mannitol, assumed to be 3-*O*-benzoyl-D-mannitol since benzoyl migration would not be expected under these mild conditions, in a somewhat lower yield (34%). Moreover, reaction time had to be increased substantially. These observations suggest that the benzoyl group inhibits reaction, possibly as a result of steric hindrance. The deacetonation procedure was also applied to 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose. Unfortunately the reaction product was a sirup which has not crystallized. Benzoylation and subsequent chromatography also failed to yield a crystalline product.

Further studies on the compounds described in this paper and on related systems are in progress.

Experimental[9]

3-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol.—An amount of 50 g. (0.191 mole) of 1,2:5,6-di-*O*-isopropylidene-D-mannitol[2] was dissolved in 100 ml. of anhydrous pyridine (prepared by refluxing for 5 hr. with barium oxide, distilling and storing over calcium hydride). After the resulting solution was cooled to 0°, benzoyl chloride (23 ml., 0.196 mole) was added slowly with agitation. The reaction mixture, after standing overnight at room temperature, was poured into 500 ml. of ice and water with vigorous stirring. In approximately an hour, an amorphous solid separated, which upon filtration and air-drying weighed 55 g.

Crystalline 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol was first obtained following chromatography. An amount of 0.2 g. of the amorphous solid, dissolved in 20 ml. of benzene, was placed on a column (190 × 33 mm., diam.) of acid-washed[10] Magnesol[11]-Celite[12] (5:1, by wt.) and developed with 500 ml. of benzene containing 2.5 ml. of *t*-butyl alcohol. Streaking the extruded column with a permanganate reagent[13] located three zones at 18–37 mm., 81–92 mm. and 120–190 mm. from the top. Elution was effected with acetone. The top zone contained 0.01 g. of a sirup, which crystallized upon the addition of petroleum ether (b.p. 60–110°), m.p. 117–120°, alone or admixed with di-*O*-isopropylidene-D-mannitol. The middle zone contained 0.12 g. of a sirup, which crystallized to yield 0.1 g. of a compound, m.p. 104–106°. The sirup (0.05 g.) from the lower zone did not crystallize.

A major portion of the amorphous solid crystallized from ethanol, upon seeding with the crystalline compound obtained from the middle zone; yield 32 g. (46%), m.p. 104–107°. Several recrystallizations from absolute ethanol gave an analytical sample, m.p. 106.5–107.5°, $[\alpha]^{22}\mathrm{D}$ $-8.5°$ (*c* 2.6, chloroform).

Anal. Calcd. for $C_{12}H_{21}O_6$-C_6H_5CO: C, 62.28; H, 7.15; C_6H_5CO, 29.3. Found: C, 62.86; H, 7.22; C_6H_5CO, 28.6.

4-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-D-arabo-3-hexulose.—Chromium trioxide (18 g.) was added in small portions to 200 ml. of anhydrous pyridine with mechanical stirring. A slight suction was applied to the reaction flask to decrease the concentration of pyridine vapor, which upon contact with solid chromium trioxide often detonated. To the resulting chromium trioxide–pyridine mixture, 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol (15 g.) dissolved in 30 ml. of pyridine was added. The reaction mixture was heated on a water-bath (bath temp. 60°) for 8 hr. with continuous stirring and then poured into 500 ml. of ice and water. The resulting mixture was extracted six times

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(3) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

(4) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952), and later papers.

(5) S. Sussman, *Ind. Eng. Chem.*, **38**, 1228 (1946).

(6) W. H. Wadman, *J. Chem. Soc.*, 3051 (1952).

(7) J. E. Cadotte, F. Smith and D. Spriestersbach, THIS JOURNAL, **74**, 1501 (1952).

(8) A product of Rohm and Haas Co., Philadelphia, Pa.

(9) All melting points are corrected. Elemental analyses were made by Drs. G. Weiler and F. F. Straus, Oxford, England.

(10) J. M. Sugihara and M. L. Wolfrom, THIS JOURNAL, **71**, 3509 (1949).

(11) A product of Westvaco Chlorine Products Co., So. Charleston, W. Va.

(12) A siliceous filter-aid produced by Johns-Manville Co., New York, N. Y.

(13) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

with ether (500-ml. portions). The combined ethereal extractions were washed successively twice with 3 *N* hydrochloric acid, with saturated, aqueous sodium bicarbonate and with water. The ether solution was dried over anhydrous sodium sulfate and concentrated under reduced pressure on a water-bath to a sirup (12 g.), which crystallized upon the addition of ethanol (15 ml.) and a seed crystal; yield of 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose, 5.5 g. (37%), m.p. 91–94°. An additional 0.5 g. of the product as well as 3 g. of starting material was obtained from the mother liquor. Correcting for these two items, the yield increases to 50%.

Seed crystals were obtained by dissolving 0.1 g. of the sirup in 20 ml. of benzene and adding the resulting solution onto the top of a column (190 × 33 mm., diam.) of acid-washed Magnesol–Celite (5:1, by wt.). The chromatogram was developed with 600 ml. of benzene–*t*-butyl alcohol (200:1, by vol.). After the column was extruded, the main zone (106–119 mm. from the top) was located by a permanganate streak. Elution was effected with acetone. The main zone contained a sirup (0.05 g.), which crystallized upon the addition of 0.5 ml. of ethanol, m.p. 93–95°.

An analytical sample of the compound was obtained by recrystallizing several times from absolute ethanol; m.p. 94–95°, $[\alpha]^{22}\text{D}$ +9.15° (*c* 1.77, chloroform).

Anal. Calcd. for $C_{19}H_{24}O_7$: C, 62.62; H, 6.64. Found: C, 62.83; H, 6.67.

The infrared spectrum was determined using a Perkin–Elmer infrared recording spectrophotometer, model 21. An absorption peak at 5.80 μ was noted and attributed to the presence of carbonyl groups. No absorption was observed at 2.66–2.96 μ, where the hydroxyl peak is normally located.

The phenylhydrazone of the ketose was prepared by dissolving 1.0 g. of 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose and 0.32 g. of phenylhydrazine in 50 ml. of methanol and refluxing for 2 hr. When most of the solvent was removed, the phenylhydrazone crystallized; yield 0.85 g. (68%), m.p. 110–120°. An analytical sample was obtained after several recrystallizations from ethanol; m.p. 131–132.5°, $[\alpha]^{22}\text{D}$ +293° (*c* 1.46, chloroform).

Anal. Calcd. for $C_{25}H_{30}O_6N_2$: C, 66.06; H, 6.65. Found: C, 65.70; H, 6.45.

Reduction of 4-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose.—A mixture of 1.6 g. of lithium aluminum hydride in 350 ml. of anhydrous ether was stirred mechanically for an hour. A solution of 10 g. of 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose in 200 ml. of anhydrous ether was then added at a rate sufficient to maintain gentle reflux in the reaction flask. After addition was completed, the reaction mixture was stirred for an additional hour. Enough water was added to destroy the surviving lithium aluminum hydride and to precipitate the aluminum salts formed, without forming a distinct aqueous layer. The ether solution was decanted, and the residue was extracted six times with 30-ml. portions of ether. The combined ether solution was concentrated on a water-bath under reduced pressure to a sirup (8.8 g.), which was redissolved in 400 ml. of hot petroleum ether (b.p. 60–110°). Upon cooling, a crystalline solid precipitated from the solution; yield 2.5 g., m.p. alone or admixed with authentic 1,2:5,6-di-*O*-isopropylidene-D-mannitol 121–123°. The filtrate was concentrated under reduced pressure to a sirup (6.3 g.), which crystallized in part. Two types of crystals were noted in this sirup, the long thread-like crystals of the di-*O*-isopropylidene-D-mannitol and small colorless prisms, m.p. 59–64°.

A portion (4.2 g.) of the sirup containing the mixed crystals, dissolved in 30 ml. of benzene, was placed on a column (255 × 75 mm., diam.) of Magnesol–Celite (5:1, by wt.) and developed with 4000 ml. of sulfuric acid-washed benzene containing 30 ml. of *t*-butyl alcohol. A permanganate streak indicated the presence of three zones on the column located at 9–25 mm., 33–81 mm. and 240–246 mm. from the top of the column. The column was sectioned accordingly, and each section was eluted with acetone. Upon evaporation of acetone, the eluate from the top section yielded 0.77 g. of crystals, m.p. 116–120°. After a single recrystallization from petroleum ether the compound did not depress the melting point of 1,2:5,6-di-*O*-isopropylidene-D-mannitol. From the lower section a sirup (0.6 g.) was obtained, which was presumed to be benzyl alcohol. The middle section contained 2.33 g. of a sirup, which crystallized upon cooling in an ice-bath. Ten milliliters of petroleum ether (b.p. 30–60°) was added to the crystalline mass, and the particles were triturated with a stirring rod. After filtration and washing with petroleum ether, the solids weighed 2.1 g., m.p. 63–65°. An analytical sample of 1,2:5,6-di-*O*-isopropylidene-D-talitol was obtained after two recrystallizations from petroleum ether (b.p. 30–60°), m.p. 64.5–65.5°, $[\alpha]^{22}\text{D}$ +5.2° (*c* 2.4, chloroform).

Anal. Calcd. for $C_{12}H_{22}O_6$: C, 54.96; H, 8.45. Found: C, 54.87; H, 8.26.

Another chromatogram of the remaining sirup (2.1 g.) from the reduction gave 0.38 g. of the di-*O*-isopropylidene-D-mannitol and 1.01 g. of the di-*O*-isopropylidene-D-talitol. The total weight of the two isomers obtained in crystalline form by fractional crystallization and by chromatography was 6.76 g. (94%).

Hydrolysis of 1,2:5,6-Di-*O*-isopropylidene-D-talitol.—To 100 ml. of reagent-grade acetone and distilled water (3:1 by vol.) was added 2 g. of 1,2:5,6-di-*O*-isopropylidene-D-talitol and 8 g. of Amberlite IR-120.[8] After the mixture was heated under reflux on a water-bath (bath temp. 55–57°) for 6 hr., the resin was removed by filtration. When the filtrate was concentrated on a water-bath (80–85°) aided by a jet of compressed air and finally under reduced pressure, an amber-colored sirup (1.2 g.) was obtained. An amount of 0.7 g. of the sirup was dissolved in ethanol with warming to effect solution. Upon cooling, light buff-colored crystals of D-talitol precipitated, which were filtered and washed with cold ethanol; yield 0.4 g. (49%), m.p. 84–88°. A single recrystallization from ethanol gave a pure white sample of D-talitol, m.p. 88–89°, $[\alpha]^{22}\text{D}$ +3.7° (*c* 10.2, water) (reported[14] m.p. 86°, $[\alpha]^{18}\text{D}$ +3.05° (*c* 10, water).

The tribenzylidene derivative of D-talitol was prepared using the general procedure of Fischer.[15] Five recrystallizations from ethanol did not narrow the melting point range of this compound, m.p. 203–207°, $[\alpha]^{22}\text{D}$ −38° (*c* 0.44, chloroform) (reported sinters 200°, m.p. 210°[15]; $[\alpha]\text{D}$ −40° (*c* 0.5, chloroform[16]).

In an attempted preparation of D-talitol hexacetate, the polyol was treated with acetic anhydride and pyridine in the usual fashion. The sirup obtained was found to be chromatographically homogeneous but could not be crystallized.

Deacetonation of 1,2:5,6-Di-*O*-isopropylidene-D-mannitol Using Amberlite IR-120.—Amberlite IR-120 (7 g.) was added to a solution of 1,2:5,6-di-*O*-isopropylidene-D-mannitol (5 g.) in 100 ml. of acetone and water (3:1, by vol.). The mixture was placed on a water-bath (40°) for 6 hr. After the resin was removed by filtration, the filtrate was concentrated on a water-bath, aided by a jet of air. When most of the solvents had evaporated, crystallization occurred. After the last traces of solvents were removed under reduced pressure, the D-mannitol weighed 3.4 g. (98%), m.p. 168–170°, undepressed when admixed with an authentic sample of D-mannitol.

Deacetonation of 3-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol Using Amberlite IR-120.—To 100 ml. of an acetone–water solution (3:1, by vol.) containing 7 g. of Amberlite IR-120, 8 g. of 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-mannitol was added with agitation. The resulting reaction mixture was heated for 22 hr. at 40°. Decreased reaction time gave a less complete reaction. The resin was removed by filtration. When the filtrate was concentrated on a water-bath, aided by a jet of air, a crystalline compound (2.1 g., 34%) was isolated, m.p. 176–178°. An analytical sample of 3-*O*-benzoyl-D-mannitol was obtained after several recrystallizations from acetone; m.p. 177.5–178.5°, $[\alpha]^{22}\text{D}$ +6.35° (*c* 2.9, pyridine).

Anal. Calcd. for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34. Found: C, 54.50; H, 6.17.

The same deacetonation procedure was applied to 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-D-*arabo*-3-hexulose. A sirup was obtained which did not crystallize. Benzoylation of this sirup and chromatography of the resulting reaction product also failed to yield a crystalline product.

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