

drous magnesium sulfate and most of the solvent was removed. The resulting precipitate was collected and boiled with 100 ml. of 95% ethanol. The remaining solid was collected to give 3-hydroxy-2,3,3-triphenylpropionanilide (VIa). The ethanol was removed from the filtrate, and the residue was treated twice more with successively smaller amounts of ethanol in the same manner, to leave in each case VIa; the total yield was 2.54 g. (16%), m.p. 193–193.5°, after two recrystallizations from 95% ethanol. Its infrared spectrum showed principal bands at 2.92, 3.31, 6.09, and 6.27  $\mu$ .

*Anal.* Calcd. for  $C_{27}H_{23}NO_2$ : C, 82.42; H, 5.89; N, 3.56. Found: C, 82.26; H, 5.74; N, 3.54.

The final ethanol extract was cooled to precipitate (two crops) 4.89 g. (58%) of recovered phenylacetamide, m.p. and m.m.p. 116–117°.

The solvent was removed from the original ethereal filtrate, and the residue was dissolved in 500 ml. of boiling petroleum ether (b.p. 30–60°). The volume of the solution was reduced, and the red oil that precipitated was discarded. The solution was cooled to precipitate 4.33 g. (60%) of recovered benzophenone, m.p. 47–48°, after recrystallization from petroleum ether. A mixture melting point with an authentic sample showed no depression.

When the experiment was repeated employing a 2-hr. condensation period, the yield of VIa was 5%.

**Dehydration of VIa to Form VIIa.**—To 10 ml. of stirred concentrated sulfuric acid at 0° was added, in small portions, 0.50 g. of VIa. After almost all of the solid had dissolved, the reaction mixture was poured into 30 g. of ice-water. The resulting milky white suspension was extracted with 200 ml. of ether. The ethereal extract was washed successively with water and saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Most of the solvent was removed, and the resulting precipitate was collected to give 0.35 g. (74%) of 2,3-diphenylcinnamanilide (VIIa), m.p. 216–217°, 218.5° after two recrystallizations from anhydrous ether. Its infrared spectrum showed principal bands at 2.95, 6.10, and 6.28  $\mu$ .

*Anal.* Calcd. for  $C_{27}H_{21}O$ : C, 86.37; H, 5.64; N, 3.73. Found: C, 86.48; H, 5.60; N, 3.54.

**Cyclization of VIIa** (0.20 g.) was effected in a mixture of 13 ml. of glacial acetic acid, 4 ml. of concentrated sulfuric acid, and 3 ml. of water (refluxed 17 hr.). The reaction mixture was diluted with water and extracted with ether. The ethereal extract was dried over anhydrous magnesium sulfate, and most of the solvent was removed. The resulting precipitate was collected to give 0.14 g. (93%) of 2,3-diphenylindenone (VIII, red prisms), m.p. 150–153°,

152–154° after recrystallization from 95% ethanol, lit.<sup>13</sup> m.p. 152–153°. A mixture melting point with an authentic sample of VIII<sup>13</sup> showed no depression and the infrared spectra of the two samples were identical.

**Condensation of Dilithiophenylacetamide with Benzophenone to Form VIIb.**—This reaction was effected and the reaction mixture was worked up essentially as described above for dilithiophenylacetamide employing 0.1 mole each of dilithiophenylacetamide and benzophenone. There was obtained 2.1 g. (7%) of 3-hydroxy-2,3,3-triphenylpropionamide (VIIb), m.p. 188–189°, 189–189.5° after recrystallization from 95% ethanol. Its infrared spectrum showed principal bands at 2.99 and 6.06  $\mu$ .

*Anal.* Calcd. for  $C_{21}H_{19}NO_2$ : C, 79.47; H, 6.03; N, 4.42. Found: C, 79.66; H, 6.02; N, 4.60.

There was recovered 88% of the starting phenylacetamide and 81% of the benzophenone.

**Dehydration of VIIb to Form VIIc.**—This reaction was effected essentially as described for the dehydration of VIa. The reaction mixture was poured onto crushed ice, and the resulting precipitate was collected and recrystallized from 95% ethanol to give (two crops) 0.40 g. (85%) of 2,3-diphenylcinnamamide (VIIc), m.p. 223–226°, 232–232.5° after two additional recrystallizations, lit.<sup>12</sup> m.p. 223°. Its infrared spectrum showed principal bands at 3.00, 3.23, and 6.13  $\mu$ .

*Anal.* Calcd. for  $C_{21}H_{17}NO$ : C, 84.25; H, 5.73; N, 4.68. Found: C, 84.02; H, 5.62; N, 4.68.

**Cyclization of VIIc** (0.10 g.) was effected as described for that of VIIa to give 0.07 g. (80%) of red 2,3-diphenylindenone (VIII), m.p. 152–154°, not depressed on admixture with an authentic sample of VIII.<sup>13</sup> The infrared spectra of the two samples were identical.

**Benzoylation of Dipotassiophenyl Acetate.**—To a stirred suspension of 0.1 mole each of dipotassiophenyl acetate and potassium amide was added 0.2 mole of methyl benzoate in 100 ml. of dry ether. After 1.5 hr., the ammonia was replaced by ether. The resulting ethereal suspension was poured into 10% hydrochloric acid. The solvent was removed from the ethereal layer, and the residue was fractionally distilled *in vacuo* to give 13.6 g. (50%) of recovered methyl benzoate, b.p. 80° at 8.6 mm., and 19.7 g. of material, b.p. 138–165° at 8.6 mm. The latter fraction, which solidified, was shaken with 5% sodium hydroxide. The insoluble material was collected to give 4.4 g. (22%) of desoxybenzoin, identified by the mixture melting point method. The alkaline filtrate was acidified to precipitate 9.7 g. (71%) of recovered phenylacetic acid.

## An Inositol Analog Containing One Sulfur Atom (Mercaptocyclohexanepentol). Synthesis and Nuclear Magnetic Resonance Characterization of Derivatives<sup>1,2</sup>

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Reaction of 1,2-anhydro-*cis*-inositol diketal with benzyl mercaptan gave a benzylmercaptopentol diketal, which was reduced to the mercaptopentol diketal. Hydrolysis of the latter gave *meso*-6-mercapto-6-deoxy-*epi*-inositol, m.p. 180° (hexaacetate, 182°). Desulfurization produced *cis*-cyclohexanepentol, confirming the configuration. The mercaptopentol diketal on acetonation gave the triisopropylidene derivative (oxathiolane), which contains a new tetracyclic ring system. The same diketal on acetylation gave an *O,S*-diacetate, which also can be prepared directly from the anhydro diketal by reaction with thiolacetic acid. Acidic hydrolysis of the diketal diacetate gives the mercaptopentol. N.m.r. and infrared spectra were used to characterize the new compounds prepared.

The synthesis and n.m.r. characterization of the first sulfur analogs of inositol were recently reported.<sup>3c</sup> These analogs were dimercapto derivatives (I) of cyclohexanetetrol (dideoxyinositol). We now have ex-

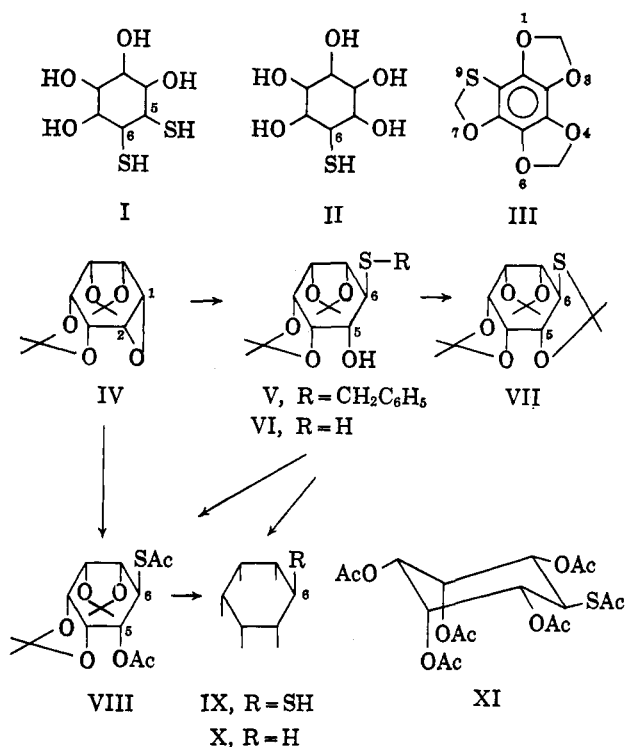
tended this investigation to the mercapto derivatives (II) of cyclohexanepentol (deoxyinositol or quercitol).

The new analogs containing a single sulfur atom are of interest for their possible inositol or anti-inositol

(1) Presented by G. E. McCasland to the Symposium on Thio Derivatives of Carbohydrates at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

(2) Paper XVII on Cyclitol Stereochemistry by G. E. McCasland and co-workers; for preceding paper, see *J. Am. Chem. Soc.*, **85**, 2866 (1963).

(3) (a) G. E. McCasland, S. Furuta, L. F. Johnson, and J. N. Shoolery *J. Am. Chem. Soc.*, **83**, 2335 (1961); (b) **83**, 4243 (1961); (c) (with A. Furst), *J. Org. Chem.*, **28**, 456 (1963); (d) **28**, 894 (1963); (e) H. Eagle and G. E. McCasland, *Biochemistry*, **2**, 1125 (1963); (f) G. E. McCasland, S. Furuta, L. F. Johnson, and J. N. Shoolery, *J. Am. Chem. Soc.*, submitted for publication; (g) G. E. McCasland, S. Furuta, and A. Furst, *ibid.*, **85**, 2866 (1963).



activity in biological systems,<sup>4</sup> as intermediates for cyclitol syntheses, and as model compounds for the application of n.m.r.<sup>5a-c</sup> and other new physical methods to carbohydrates. We also plan to use them for a series of chemical studies on the competitive reactions and interactions of mercapto and hydroxyl groups situated on the same alicyclic ring.

The most convenient route to dimercapto analogs was previously found to be the lithium aluminum hydride reduction of a trithiocarbonate diketal, obtained by reaction of an anhydro inositol diketal with potassium methyl xanthate.<sup>5,3c</sup> Our first successful preparation of a monomercapto analog was based on the sodium-liquid ammonia reduction of a benzylmercaptopentol diketal (V) obtained by reaction of an anhydro inositol diketal with benzyl mercaptan.<sup>6-8</sup>

The diketal<sup>9a</sup> (IV) of 1,2-anhydro-*cis*-inositol reacted in the expected manner to give a 75% yield of the crystalline, sharp-melting benzylmercaptopentol diketal (V). From the assumed mechanism, rearward attack by benzylmercaptide ion on oxirane carbon, this product would have the racemic (12345/6) configuration, corresponding to that of (*meso*) *epi*-inositol. The n.m.r. and infrared spectra were consistent with the assigned structure.

The sodium-ammonia reduction<sup>6</sup> of the *S*-benzyl derivative gave a surprisingly good (88%) yield of the mercaptopentol diketal (VI) assumed to have the same configuration. This colorless, odorless product had a

(4) For a discussion of certain biological aspects of this research, see (a) *Chem. Eng. News*, **40**, 51 (April 9, 1962); (b) T. Posternak, "Les Cyclitols," Hermann, Paris, France, 1962, part II; (c) G. E. McCasland, *J. Am. Chem. Soc.*, **85**, 2189 (1963).

(5) L. Owen, et al., *J. Chem. Soc.*, 1024 (1960); 1030 (1960).

(6) For similar preparations of mercaptodeoxy monosaccharides by the *S*-benzyl synthesis, see N. Jamieson and R. Brown, *Can. J. Chem.*, **39**, 1765 (1961).

(7) A product of Evans Chemetics, Inc., New York 17, N. Y. We would like to thank Evans Chemetics for a generous sample of benzyl mercaptan ( $\alpha$ -toluenethiol).

(8) The ketals mentioned here are normal acetonation products.

(9) (a) S. J. Angyal, et al., *J. Chem. Soc.*, 3691 (1957); (b) *Chem. Ind. (London)*, 947 (1955); (c) *J. Chem. Soc.*, 3682 (1957).

sharp melting point and an appropriate infrared spectrum. It was anticipated that the neighboring free hydroxyl group in V might interfere by forming an insoluble sodium alkoxide. No such difficulty was encountered, but such a reaction might fail if several free hydroxyl groups were present. Electron feed-in from the highly negative alkoxide oxygen may or may not assist the reduction, depending on the mechanism.

In solution any compound, such as VI, containing a free mercapto group might be oxidized by atmospheric oxygen to a disulfide, especially above pH 7. To avoid this complication, all experiments involving such compounds were conducted under oxygen-free nitrogen.

Mild acidic hydrolysis of the diketal (VI) gave a good yield of the desired inositol analog (IX). This mercaptopentol is a colorless, odorless, water-soluble crystalline substance. It is surprisingly sharp-melting (with decomposition) for a polyol, and appears to be indefinitely stable in the dry, solid state.

For a mercaptocyclohexanepentol, 20 diastereomeric configurations (8 *meso*, 12 active) are possible, as for other substituted cyclohexanes of the type C<sub>6</sub>H<sub>6</sub>A<sub>5</sub>B. The actual configuration was established by desulfurization with Raney nickel,<sup>10</sup> which gave *meso-cis*-quercitol (cyclohexanepentol) (X). This indicates that the new mercaptopentol is either 1-mercapto-1-deoxy-*cis*-inositol or 6-mercapto-6-deoxy-*epi*-inositol (IX), and from the assumed mechanisms only the latter configuration is probable. The intermediates V, VI, VII, and VIII no doubt have the same configuration.

This is a new method of synthesis for *cis*-quercitol (X) which previously was prepared from quinonetetrol,<sup>9b,9c</sup> from *cis*-inosose,<sup>9b,9c</sup> and from 1,2-anhydro-*cis*-inositol<sup>11</sup> (made by hydrolysis of diketal, IV). The identity of our new preparation was established by infrared spectra and a mixture melting point. The n.m.r. spectrum of *cis*-quercitol was for the first time recorded (see Experimental), but configurational interpretation has not been accomplished.

The hexaacetate derivative of the mercaptopentol (IX) was prepared directly from the diketal (VI) by heating with aqueous acetic acid, adding excess acetic anhydride, and heating again.<sup>12</sup> The hexaacetate is water-insoluble and its other properties are appropriate.

The diketal (VI) is converted by acetic anhydride in pyridine to the *O,S*-diacetate (VIII). The same diacetate can be obtained *directly* from the anhydro diketal (IV) by reaction with thiolacetic acid. The steps IV  $\rightarrow$  VIII and VIII  $\rightarrow$  IX provide a short cut synthesis for the mercaptopentol; however, the overall yield was only 23%, as compared with 51% for the *S*-benzyl synthesis.

The diketal (VI) is converted by acetone to the triisopropylidene derivative (VII). This oxathiolane diketal contains a new tetracyclic 5,5,5,6 ring system,

(10) For a review on desulfurization with Raney nickel catalyst, see *Chem. Rev.*, **62**, 347-404 (1962).

(11) G. E. McCasland, S. Furuta, and V. Bartuska, *J. Org. Chem.*, **28**, 2096 (1963).

(12) The n.m.r. sample (but not the microanalytic sample) of the hexaacetate appeared to contain some diketal diacetate impurity, as indicated by three relatively small ketal methyl singlets at 1.38, 1.55, and 1.70 p.p.m. This suggests that ketal hydrolysis was not always complete under the usual mild conditions employed. It is also conceivable that one of the *O,O*-isopropylidene groups migrates during hydrolysis to an *O,S*-position, where hydrolysis would be more difficult. This possibility is being investigated.

not listed as such or as its aromatic parent (III) in the "Ring Index."<sup>13</sup>

The acetonation of VI also might lead to products not containing an oxathiolane ring. Thus benzaldehyde reportedly<sup>14</sup> combines with 2 moles of 2-mercaptoethanol to give a mercaptal diol of the type  $\text{RCH}(\text{SCH}_2\text{CH}_2\text{OH})_2$ . Products of the type  $\text{RCH}(\text{OCH}_2\text{CH}_2\text{SH})_2$  are also conceivable. However the analytical and infrared data demonstrate that our own product has the structure VII. The experimental results suggest that the *trans*-fused cyclohexaneoxathiolane ring system is strainless, or nearly so.

Infrared spectra were recorded for every new compound. A free mercapto group was indicated by characteristic weak S—H stretching absorption at about  $2600\text{ cm.}^{-1}$ . Hydroxyl or acetoxy groups were recognized by their well-known O—H and C=O stretching absorption peaks.

N.m.r. spectra were used to characterize several of the intermediates. The n.m.r. spectrum of the benzylmercaptopentol diketal (V, see Experimental), confirmed the presence of the free hydroxy and benzylmercapto groups, and the two dioxolane ketal rings.

The spectrum of the mercaptopentol diketal (VI) showed ketal methyl signals at 1.38 (6 protons) and 1.55 p.p.m. (6 protons). A signal for the single —SH proton appeared at 2.1 and for the —OH proton at 2.6 p.p.m. The latter signal was abolished by adding a little deuterium oxide. The signals for the six ring protons in the region 3.3–4.7 p.p.m. have not been fully interpreted.

In the spectrum for the diketal *O,S*-diacetate (VIII) the signal for one of the ketal methyl groups (3 protons) was shifted downfield from 1.55 to 1.70 p.p.m., probably because of a change in environment due to the nearby *O*-acetate group, or because of some distortion in conformation. An *O*-acetate methyl singlet (3 protons) appeared at 2.09, and an *S*-acetate methyl singlet (3 protons) at 2.35 p.p.m. Signals for the six ring protons in the region 3.4–5.0 p.p.m. have not been fully interpreted.

The spectrum of the hexaacetate<sup>12</sup> is of interest, since it is free to assume a relatively strainless chair conformation, XI, unlike the diketal derivatives. The (presumably equatorial) *S*-acetate methyl peak (3 protons) appeared as before at 2.35 p.p.m. However, the *O*-acetate methyl pattern was split into a 6-proton peak (2.19 p.p.m.) and a 9-proton peak (2.00 p.p.m.). We conclude tentatively that the 2.19 peak is due to two axial *O*-acetate groups, and the 2.00 peak to three equatorial *O*-acetate groups. This interpretation would be consistent with configuration XI, assigned on the basis of chemical correlations, but not in itself sufficient to prove this configuration. Configurational interpretation of the signals due to the six ring protons (4.2–5.7 p.p.m.) has not been accomplished.

Work on similar syntheses starting with benzyl mercaptan and other diastereomers of anhydroinositol diketal is in progress.<sup>15</sup> The anhydro diketal (IV) on reaction with potassium methyl xanthate surprisingly

is converted to a cyclohexenetetrol diketal<sup>15</sup> (not a trithiocarbonate diketal). Details of these experiments will be reported elsewhere.

## Experimental

All melting points have been corrected, and unless noted otherwise, were measured on a Nalge-Axelrod micro hot stage. Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Illinois. N.m.r. spectra were recorded and integrated with a Varian A-60 high resolution spectrometer. Chloroform-*d* was used as solvent, with a tetramethylsilane internal reference, and chemical shifts are expressed as  $\delta$  values (p.p.m.), unless noted otherwise. Infrared spectra using potassium bromide pellets were measured on a Perkin-Elmer, Model 137, Infracord recording spectrometer. Darco G-60 decolorizing charcoal<sup>16</sup> was used. Petroleum ether of boiling range 65–110° was used. All solutions containing products (or starting materials) with free mercapto groups were protected by passage of a current of dry, oxygen-free nitrogen. Atmospheric moisture was excluded from all apparatus containing anhydrous reagents or solvents.

**DL-(12345/6) Diastereomer of 6-Benzylmercapto-1,2:3,4-di-*O*-isopropylidene-1,2,3,4,5-cyclohexanepentol (V).**—To 485 mg. of 1,2-anhydro-3,4:5,6-di-*O*-isopropylidene-*cis*-inositol<sup>16</sup> (m.p. 143°) was added a solution of 260 mg. of benzylmercaptan and 200 mg. of metallic sodium in 8.0 ml. of absolute ethanol. The mixture was boiled at reflux for 2 hr., then evaporated.

The semisolid residue was distributed between benzene and water (40 ml. of each), and the suitably processed benzene phase treated with charcoal, and evaporated.

The residual light yellow sirup was taken up in cyclohexane (3–4 ml.). The solution (treated with charcoal) on standing yielded 470 mg. of colorless crystals, m.p. 76–79°. Second and third crops of 100 mg. and 20 mg. were obtained (m.p. 77–79°, 76–80°).

The combined crops were recrystallized from 2:1 cyclohexane-petroleum ether, giving 520 mg. of colorless, fine needles, m.p. 85–86°. Including a 30-mg. second crop of the same melting point; the yield was 75%.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{26}\text{O}_9\text{S}$ : C, 62.27; H, 7.15; S, 8.75. Found: C, 61.86; H, 7.03; S, 8.83.

The n.m.r. spectrum was recorded. The nine protons of three methyl groups produced a sharp singlet at  $\delta = 1.33$  p.p.m., and the three protons of the remaining methyl group produced a sharp singlet at 1.53 p.p.m. The five aromatic protons produced a pattern with three or more peaks in the region 7.2–7.5 p.p.m. The six ring protons produced a complex pattern in the region 3.9–4.6 p.p.m. The two methylene protons gave a poorly resolved pattern at 3.2–3.5 p.p.m. The hydroxyl proton gave a pattern in the region 2.30–2.60 p.p.m., which was abolished by addition of a drop of deuterium oxide. The HDO signal then appeared as a sharp singlet at 4.55 p.p.m.

**DL-(12345/6) Diastereomer of 1,2:3,4-Di-*O*-isopropylidene-6-mercapto-1,2,3,4,5-cyclohexanepentol (VI).**—To a mixture of 500 mg. of the *S*-benzyl derivative (m.p. 86°) with 30 ml. of liquid anhydrous ammonia, in a Dry Ice-acetone cooling bath, were added small pieces of sodium metal with stirring, until the blue color persisted for 20 min. Powdered ammonium chloride was gradually added until the blue color disappeared.

The ammonia was evaporated, and the residue was extracted with anhydrous chloroform. The filtered chloroform solution was evaporated. The crystalline residue was taken up in hot 2-propanol (filter). On standing the solution yielded 270 mg. of colorless crystals, m.p. 158–159°; including a 60-mg. second crop (m.p. 157–158°), the yield was 87%.

The infrared spectrum showed a characteristic weak peak due to an —SH group at  $2550\text{ cm.}^{-1}$ . The n.m.r. spectrum was recorded.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{20}\text{O}_5\text{S}$ : C, 52.15; H, 7.30; S, 11.60. Found: C, 52.26; H, 7.47; S, 11.52.

**DL-(12345/6) Diastereomer of 1,2:3,4-Di-*O*-isopropylidene-6-mercapto-1,2,3,4,5-cyclohexanepentol 5-*O*-6-*S*-Diacetate (VIII).**  
**A. From the Mercaptopentol Diketal.**—A 55-mg. portion of the mercaptopentol diketal (m.p. 159°) and 45 mg. of redistilled acetic anhydride were dissolved in 0.6 ml. of anhydrous pyridine. After 3 days, 5.0 ml. of chloroform was added, and the resulting

(13) A. Patterson, L. Capell, and D. Walker, "The Ring Index," 2nd Ed., American Chemical Society, Washington, D. C., 1960, pp. 541–546.

(14) E. Fromm and H. Jörg, *Ber.*, **58**, 304 (1925); E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., New York, N. Y., 1958, p. 379.

(15) S. Furuta, unpublished work.

(16) A product of the Darco Division, Atlas Powder Co., Wilmington Del.

solution was washed with 5% sodium bicarbonate solution (5.0 ml.). The chloroform phase was processed in the usual manner, and the crude product recrystallized from 2-propanol (filter), giving 60 mg. (83%) of colorless crystals, m.p. 147–148°.

*Anal.* Calcd. for  $C_{18}H_{24}O_7S$ : C, 53.32; H, 6.71; S, 8.89. Found: C, 53.20; H, 6.62; S, 9.11.

**B. From the Epoxide Diketal.**—A mixture of 120 mg. of the epoxide diketal (m.p. 143°), 85 mg. of thioacetic acid, and 2.0 ml. of anhydrous pyridine was boiled under reflux for 4 hr. The red-brown solution was evaporated. Dry toluene was added to the sirupy residue, and evaporation was repeated. The residual sirup was taken up in 3–5 ml. of 9:1 cyclohexane–chloroform (treated with charcoal). The solution on standing deposited 100 mg. of crystals which had an orange discoloration, m.p. 133–137°.

This material was dissolved in 1.5 ml. of 8:2 cyclohexane–chloroform and passed through a column (80 × 6 mm.) of Woelm activity grade I neutral aluminum oxide.<sup>17</sup> The column was eluted with 30 ml. of 8:2 cyclohexane–chloroform. The eluate on evaporation gave 85 mg. of crystalline product, which was recrystallized from 9:1 cyclohexane–chloroform, giving 60 mg. (33%) of colorless crystals, m.p. 146–148°. The infrared spectrum was identical with that of an authentic sample (see A), and a mixture melting point was not depressed.

The diketal diacetate melting point is similar to that of the diketal itself. The two compounds may be distinguished by the strong *S*-acetate and *O*-acetate C=O stretching absorption at 1720, 1750  $cm^{-1}$ , found only in the diacetate infrared spectrum; and the S—H and O—H stretching absorption at 2550 and 3600  $cm^{-1}$ , found only in the diketal spectrum.

The n.m.r. spectrum was recorded.

*meso*-(12345/6) Diastereomer of 6-Mercapto-1,2,3,4,5-Cyclohexanepentol (6-Mercapto-6-deoxy-*epi*-inositol, IX). **A. From the Diketal.**—A mixture of 55 mg. of the diketal (m.p. 159°) with 2.0 ml. of water and a drop of formic acid was heated at 90–100° for 1 hr. The solution was evaporated. Absolute ethanol was added to the residue, and evaporation was repeated. The residue was taken up in 2.0 ml. of 95% ethanol (filter). The solution on standing deposited 25 mg. of colorless, odorless, water-soluble crystals, m.p. 179–180°. Including a 5-mg. second crop (m.p. 178–179°), the yield was 77%.

*Anal.* Calcd. for  $C_8H_{12}O_5S$ : C, 36.72; H, 6.17; S, 16.34. Found: C, 36.39; H, 6.36; S, 15.97.

**B. From the Diketal Diacetate.**—A solution of 40 mg. of the diketal diacetate (m.p. 148°) in 2.0 ml. of hot 1 *N* hydrogen chloride in 50% (v./v.) ethanol was boiled under reflux for 4 hr. The solution (treated with charcoal) was evaporated. To the colorless solid residue was added 1.0 ml. of ethanol, and the evaporation was repeated; the addition and evaporation were again repeated. The residue was recrystallized from 95% ethanol, giving 14 mg. (65%) of product, m.p. 177–179°. Identity of the product with the above mercaptopentol was demonstrated by comparison of infrared spectra and by a mixture melting point.

*meso*-(12345/6) Diastereomer of 6-Mercapto-1,2,3,4,5-cyclohexanepentol Hexaacetate (XI).—A mixture of 138 mg. of the mercaptopentol diketal (m.p. 159°) with 0.1 ml. of water and 1.0 ml. of acetic acid was heated at 90–100° for 30 min. Acetic anhydride (3.0 ml.) was then added, and the solution was boiled

under reflux for 5 hr. After the first hour, 20 mg. of fused sodium acetate was added.

The product was isolated in the usual manner and recrystallized from 2-propanol, giving 120 mg. (54%) of colorless crystals, m.p. 181–182°. The hexaacetate melting point is very similar to that of the mercaptopentol itself. However, the hexaacetate infrared spectrum showed strong ester C=O and C—O stretching absorption at 1750 and 1230  $cm^{-1}$ , which were lacking in the mercaptopentol spectrum. The mercaptopentol spectrum showed S—H and O—H stretching absorption at 2550 and 3500  $cm^{-1}$ , lacking in the hexaacetate spectrum. In addition to the *O*-acetate peak at 1750, the hexaacetate showed a somewhat smaller *S*-acetate peak at 1720  $cm^{-1}$ . The n.m.r. spectrum was recorded.

*Anal.* Calcd. for  $C_{18}H_{24}O_{11}S$ : C, 48.21; H, 5.39; S, 7.15. Found: C, 48.28; H, 5.40; S, 6.93.

**Conversion of the Mercaptopentol to *cis*-Quercitol (X).**—A mixture of 25 mg. of the mercaptopentol (m.p. 180°), 100 mg. of commercial Raney nickel catalyst (probably could use less), and 20 ml. of water was hydrogenated at 25° (3 atm.) for 3 hr. The catalyst was removed by filtration, and the filtrate was evaporated. The nearly colorless residue was taken up in 1–2 ml. of hot 85% ethanol (treated with charcoal). The solution on standing deposited 15 mg. of *cis*-quercitol, m.p. 233° dec. (lit.<sup>9c</sup> m.p. 235–240° dec.). The infrared spectrum was identical with that of an authentic sample.

The n.m.r. spectrum (not previously reported) was recorded and integrated using deuterium oxide solvent and a tetramethylsilane external reference. The spectrum showed a 4-peak, 2-proton methylene pattern in the region 2.15–2.55 p.p.m., and a complex 5-proton O—C—H pattern in the region 3.9–4.7 p.p.m. The HDO peak appeared at 5.2 p.p.m. Configurational interpretation of the spectrum has not been accomplished.

*DL*-(12345/6) Diastereomer of 1,2,3,4-Di-*O*-isopropylidene-5,6-*O,S*-isopropylidene-6-mercapto-1,2,3,4,5-cyclohexanepentol (VII).—A mixture of 55 mg. of the mercaptopentol diketal (m.p. 159°) with 100 mg. of fused zinc chloride and 0.9 ml. of acetone was kept at room temperature for 4 days. To the resulting solution was added 150 mg. of anhydrous potassium carbonate in 0.2 ml. of water, with stirring. After 0.5 hr. stirring, the mixture was filtered, and the filtrate was evaporated.

The residue was taken up in 1–2 ml. of hot 2-propanol (treated with charcoal). Upon standing the solution yielded 23 mg. of colorless crystals, m.p. 154–155°. Including a 20-mg. second crop, the yield was 69%. The combined crops were recrystallized for analysis, giving 25 mg. of product, m.p. 155.5–156°.

*Anal.* Calcd. for  $C_{18}H_{24}O_8S$ : C, 56.94; H, 7.65; S, 10.10. Found: C, 56.93; H, 7.55; S, 9.96.

The melting point of the product is similar to that of the starting material; however the infrared spectrum of the product lacked the characteristic S—H and O—H peaks at 2550 and 3600  $cm^{-1}$  which were present in the starting material spectrum.

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