

*Dithiols. Part XVII.\* S-Benzyl Derivatives of 2:3-Dimercapto-  
propanol and 1:3-Dimercapto-2-propanol.*

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Reaction of 2:3-dibromopropanol or its acetate with the sodium derivative of toluene- $\omega$ -thiol results in rearrangement; the product is 1:3-bisbenzylthioprop-2-ol, which is also obtained by selective benzylation of 1:3-dimercapto-2-propanol. 2:3-Bisbenzylthioprop-2-ol is similarly prepared from 2:3-dimercapto-2-propanol, and the structures of both bisbenzyl compounds are established by reduction to the dimercapto-alcohols and desulphurisation of the latter. The infrared absorption spectra of 1:3-bisbenzylsulphinylpropan-2-ol and of 1:3-bisbenzylsulphonylpropan-2-ol are discussed. The synthesis of 2:3-bisbenzylthiopropyl 2:3:4:6-tetra-*O*-acetyl- $\beta$ -D-glucoside is described.

DIFFICULTIES which arise in the isolation of polyhydroxy-derivatives of 2:3-dimercapto-2-propanol (BAL) (I) and of other dithiols have been attributed to the occurrence of side-reactions, probably involving cyclisation, during deacetylation of the fully-acetylated compounds (Harding and Owen, *J.*, 1954, 1536). If the thiol groups were protected in some other way than as acetylthio-functions, such that removal of *O*-acetyl groups could precede the regeneration of free thiol, then cyclisation (which involves attack by -SH on  $\geq\text{C-OAc}$ ) should be avoided. The present paper describes some exploratory experiments involving protection by benzyl groups, and eventual regeneration of the free thiol by hydrogenolysis (cf. "Organic Reactions," Vol. VII, p. 263). For the present investigation, 2:3-bisbenzylthioprop-2-ol (II) was chosen as a model substance; Stocken (*J.*, 1947, 592) mentioned that BAL could be regenerated from it by treatment with sodium in liquid ammonia, but no details were given.

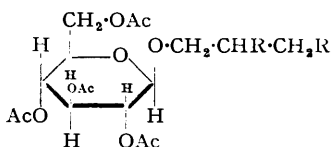
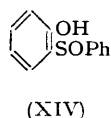
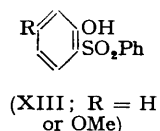
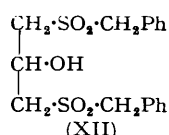
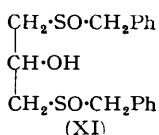
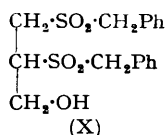
Kostir and Kral (*Coll. Czech. Chem. Comm.*, 1949, **14**, 219) attempted the preparation of the acetate of (II) by reaction of 2:3-dibromopropyl acetate (III) with the sodium derivative of toluene- $\omega$ -thiol, but they obtained only an impure product which decomposed with the formation of stilbene when distilled at 0.5 mm.; the stilbene was presumably formed from dibenzyl disulphide, which is known to yield the hydrocarbon when strongly heated (Fromm and Achert, *Ber.*, 1903, **36**, 534). In our hands the replacement reaction occurred very readily in ethanol, and the product distilled at low pressure without decomposition, no stilbene being encountered; the material, however, was found to be largely deacetylated, solvolysis presumably having occurred under the basic conditions of the experiment. Deacetylation was therefore completed catalytically with ethanolic sodium ethoxide, and the resulting analytically pure bisbenzylthioprop-2-ol was characterised as the crystalline  $\alpha$ -naphthylurethane; reacetylation of the bisbenzylthioprop-2-ol gave the acetate as a liquid.

As an alternative route to the same compound, the selective benzylation of BAL in aqueous sodium hydroxide, with 2 mol. of benzyl chloride, was investigated. This gave a bisbenzylthioprop-2-ol in excellent yield, but the crystalline  $\alpha$ -naphthylurethane was different from that obtained by the other route, and the liquid acetates, also, were not identical. A rearrangement had evidently occurred in one of the preparations, and although it was very improbable that the second method had taken an unusual course it was necessary to provide a rigid proof of the structures of both di-*S*-benzyl compounds. Debenzylation of each with sodium and liquid ammonia, preferably in the presence of some ethanol, took place smoothly and gave the corresponding dimercapto-2-propanols, which in turn were desulphurised with Raney nickel, and the resulting propanol identified by oxidation and characterisation of the propaldehyde or acetone as the 2:4-dinitrophenylhydrazone. In this way the dibenzyl compound obtained by benzylation of BAL gave

\* Part XVI, Johary and Owen, preceding paper.



reaction after a few minutes gave the disulphoxide (XI), whilst under more vigorous conditions the disulphone (XII) was obtained. Fromm, Kapeller, and Taubmann (*loc. cit.*) claimed to have obtained the latter by permanganate oxidation of 1 : 3-bisbenzylthioprop-2-ol, but stated that it crystallised from ethanol as an extremely stable monohydrate, which could not be dehydrated by recrystallisation or by drying it at 120°, but only by long boiling with acetic acid. Our product, crystallised either from ethanol or acetic acid, was anhydrous, even when water was present in the solution. Rothstein (*J.*, 1937, 309), who obtained it from a crude 1 : 3-bisbenzylthioprop-2-ol, also recorded only the anhydrous form. A feature of interest is that the disulphoxide and the disulphone have almost identical melting-points, and a mixture shows no significant depression, so



(XV; R = Br)

(XVI; R = S-CH<sub>2</sub>Ph)

that identification by mixed melting-point is not conclusive. The two compounds are most readily distinguished by their different solubility properties. Their infrared absorption spectra were determined in Nujol mull by Mr. R. L. Erskine (Organic Spectrographic Laboratory). The disulphone (XII) showed a group of bands with strong maxima at 1309, 1264, 1148, and 1131 cm.<sup>-1</sup>, and weaker peaks at 1406, 1330, 1236, 1210, 1070, 1026, and 1000 cm.<sup>-1</sup>; the hydroxyl band was at 3390 cm.<sup>-1</sup>. The main frequencies are somewhat lower than those characteristic of simple sulphones, for which the maxima are usually in the ranges 1350—1300 and 1155—1140 cm.<sup>-1</sup> (Barnard, Fabian, and Koch, *J.*, 1949, 2442; Amstutz, Hunsberger, and Chessick, *J. Amer. Chem. Soc.*, 1951, 73, 1220). The displacements, and the splitting of the main bands, are probably due to hydrogen bonding with the hydroxyl group; Amstutz *et al.* (*loc. cit.*) found displacement to lower frequencies (1138—1130 cm.<sup>-1</sup>) for two *ortho*-hydroxydiphenyl sulphones (XIII) in which the hydroxyl group has the same relationship to the sulphone group as in (XII). The spectrum of the disulphoxide (XI) was simpler than that of the disulphone, and showed no strong absorption between 1300 and 1100 cm.<sup>-1</sup>; in addition to a hydroxyl peak at 3225 cm.<sup>-1</sup>, the main bands were at 1077 and 1030 cm.<sup>-1</sup>, with weaker peaks at 1005, 995, and 976 cm.<sup>-1</sup>. Barnard *et al.* (*loc. cit.*) found a strong maximum at about 1035 cm.<sup>-1</sup> with several simple sulphoxides, and observed that in the presence of added methanol a new peak appeared at lower frequency; they concluded that sulphoxides form stronger hydrogen bonds than do sulphones. Amstutz *et al.* (*loc. cit.*) reached a similar conclusion from the behaviour of *o*-hydroxydiphenyl sulphoxide (XIV) which showed no hydroxyl band, only a weak maximum at 1034 cm.<sup>-1</sup> and a strong band at 994 cm.<sup>-1</sup>.

For a synthesis of the *O*-glucoside of BAL *via* the *S*-benzyl derivative the key compound is 2 : 3-bisbenzylthiopropyl 2 : 3 : 4 : 6-tetra-*O*-acetyl-β-*D*-glucoside (XVI). Attempts to obtain this by direct condensation of 2 : 3-bisbenzylthioprop-2-ol with acetobromoglucose were unsuccessful owing to incomplete reaction. When 2 : 3-dibromopropyl 2 : 3 : 4 : 6-tetra-*O*-acetyl-β-*D*-glucoside (XV) was treated with a large excess of the sodium derivative of toluene-ω-thiol in ethanol it was possible to effect complete replacement of the halogen atoms, but deacetylation also occurred. The resulting crude 2 : 3-bisbenzylthiopropyl β-*D*-glucoside on reacylation and fractional precipitation gave the required tetra-acetyl compound (XVI). Catalytic deacetylation, followed by debenzoylation with sodium and ethanol in liquid ammonia, gave a product with about 85% of the theoretical thiol content, though separation of the free glucoside from the inorganic material was not practicable.

## EXPERIMENTAL

**2 : 3-Bisbenzylthiopropanol.**—Benzyl chloride (27.6 g.) was gradually added (25 min.) to a vigorously stirred solution of 2 : 3-dimercaptopropanol (12.4 g.) and sodium hydroxide (9 g.) in water (60 c.c.) under nitrogen; stirring was maintained for a further hour at room temperature and for 1.5 hr. at 100°. The insoluble oil was then extracted from the cold solution with ether, and on distillation gave 2 : 3-bisbenzylthiopropanol (23.2 g.), b. p. 215—230° (bath)/0.0001 mm.,  $n_D^{20}$  1.6150 (Found : C, 66.8; H, 6.7; S, 21.4.  $C_{17}H_{20}OS_2$  requires C, 67.1; H, 6.6; S, 21.05%). The  $\alpha$ -naphthylurethane (prepared by heating it with  $\alpha$ -naphthyl isocyanate for 7 hr. at 90°) after crystallisation from benzene-petroleum (b. p. 60—80°) had m. p. 80—82° (Found : C, 70.7; H, 5.8; N, 3.0; S, 12.9.  $C_{28}H_{32}O_2NS_2$  requires C, 71.0; H, 5.75; N, 3.0; S, 13.5%). Acetylation of 2 : 3-bisbenzylthiopropanol with acetic anhydride and sodium acetate at 100° gave the acetate, b. p. 220—230° (bath)/0.0006 mm.,  $n_D^{20}$  1.5856 (Found : Ac, 12.2.  $C_{19}H_{24}O_4S_2$  requires Ac, 12.4%).

**Debenzylation.** Sodium (6 g.), in small pieces, was added to a stirred solution of 2 : 3-bisbenzylthiopropanol (8.8 g.) and ethanol (10 c.c.) in liquid ammonia (*ca.* 250 c.c.). A vigorous evolution of gas occurred, and the blue colour produced by each addition disappeared rapidly in the early stages, but persisted towards the end. The ammonia was then evaporated off on the water-bath, and the residue was treated with crushed ice (100 g.) and 10% sodium hydroxide solution (20 c.c.). Non-thiol material was removed by ether-extraction, and the alkaline solution was then acidified at 0° with concentrated hydrochloric acid and continuously extracted with ether for several hours; distillation of the oil so obtained gave 2 : 3-dimercaptopropanol (2.2 g., 61%), b. p. 90°/2 mm.,  $n_D^{20}$  1.5654 (purity by iodine titration, 95%). A portion (0.5 g.) of this product was heated on the steam-bath for 4 hr. with water (30 c.c.) and Raney nickel (*ca.* 5 g.). The filtered solution was then boiled in a distillation flask during the addition of a 6% solution of sodium dichromate in 25% sulphuric acid (10 c.c.). The distillate was collected in aqueous 2 : 4-dinitrophenylhydrazine sulphate and gave propaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 154—156°. Chromatography of the crude derivative failed to indicate the presence of any other compound.

In carrying out the debenylation in the absence of ethanol, difficulty was experienced owing to the formation of a coating around the sodium; this was overcome by transferring under pressure a solution of sodium (4.5 g.) in liquid ammonia (75 c.c.) into a solution of 2 : 3-bisbenzylthiopropanol (12 g.) in liquid ammonia (325 c.c.). The product on distillation gave 2 : 3-dimercaptopropanol (3.5 g.), b. p. 114—115°/10 mm.,  $n_D^{21}$  1.5720 (purity by iodine titration, 99%).

**1 : 3-Dibromoprop-2-yl Acetate.**—1 : 3-Dibromopropan-2-ol (*Org. Synth.*, Coll. Vol. II, 308) (25 g.) was heated with acetic anhydride (25 g.) for an hour at 130—140°. Excess of anhydride and acetic acid was then removed under reduced pressure and the residue was stirred with aqueous sodium hydrogen carbonate. The insoluble oil was isolated by ether extraction, and on distillation gave the acetate (27 g.), b. p. 106—108°/9 mm., 115—117°/20 mm.,  $n_D^{20}$  1.5037 (Found : C, 22.8; H, 3.2. Calc. for  $C_5H_9O_2Br_2$  : C, 23.1; H, 3.1%). Previous workers, using acetyl chloride, recorded b. p. 228° (Aschan, *Ber.*, 1890, **23**, 1827) and b. p. 120°/15 mm.,  $n_D^{20}$  1.5141 (Andreeva and Chernov, *Chem. Abs.*, 1940, **34**, 6572). The acetate slowly decomposes, with liberation of acetic acid, when kept.

**1 : 3-Bisacetylthioprop-2-yl Acetate.**—When freshly prepared 1 : 3-dibromoprop-2-yl acetate (20 g.), potassium thiolacetate (23 g.), and ethanol (100 c.c.) were warmed together, a vigorous reaction occurred. After this had subsided the mixture was heated and stirred on the steam-bath for 90 min., and then concentrated under reduced pressure. The residue was diluted with water (100 c.c.) and extracted with ether to give 1 : 3-bisacetylthioprop-2-yl acetate (16.8 g.), b. p. 140—145°/0.08 mm., which solidified; recrystallisation from benzene-petroleum (b. p. 60—80°) gave needles, m. p. 46—48° (Found : C, 43.2; H, 5.8; S, 25.9.  $C_9H_{14}O_4S_2$  requires C, 43.2; H, 5.6; S, 25.6%).

**1 : 3-Dimercaptopropan-2-ol.**—The above triacetyl compound (10 g.) was boiled under reflux for 2 hr. in methanol (75 c.c.) and concentrated hydrochloric acid (4 c.c.). The solvent was then removed under reduced pressure and the residue, after several evaporations with small amounts of benzene, was distilled to give 1 : 3-dimercaptopropan-2-ol (4.2 g., 85%), b. p. 68—69°/0.8 mm.,  $n_D^{23}$  1.5696 (purity by iodine titration, 99%). Rheinboldt and Tetsch (*Ber.*, 1937, **70**, 675) give b. p. 94°/12 mm.; Sjöberg (*Ber.*, 1942, **75**, 13) gives b. p. 82°/1.5 mm., 72°/0.7 mm.,  $n_D^{20}$  1.5700.

**1 : 3-Bisbenzylthioprop-2-ol.**—Treatment of 1 : 3-dimercaptopropan-2-ol (3.5 g.) with

benzyl chloride (7.5 g.), sodium hydroxide (2.5 g.), and water (15 c.c.), as described for the 1 : 2-isomer, gave 1 : 3-bisbenzylthiopropyl-2-ol (6.1 g., 75%), b. p. 230—250° (bath)/0.0005 mm.,  $n_D^{25}$  1.6100 (Found : C, 66.8; H, 6.8; S, 21.1.  $C_{17}H_{20}OS_2$  requires C, 67.1; H, 6.6; S, 21.05%). The  $\alpha$ -naphthylurethane crystallised from benzene-petroleum (b. p. 60—80°) in fibrous needles, m. p. 85° (Found : C, 71.0; H, 5.9; N, 2.8; S, 12.8.  $C_{28}H_{27}O_2NS_2$  requires C, 71.0; H, 5.75; N, 3.0; S, 13.5%); the acetate (acetic anhydride-sodium acetate) was an oil, b. p. 205—230° (bath)/0.0001 mm.,  $n_D^{25}$  1.5830 (Found : C, 65.9; H, 6.6; S, 18.4.  $C_{19}H_{22}O_2S_2$  requires C, 65.9; H, 6.4; S, 18.5%).

*Reaction of 2 : 3-Dibromopropyl Acetate with Toluene- $\omega$ -thiol.*—Freshly distilled toluene- $\omega$ -thiol (32 g.) was added to ethanolic sodium ethoxide [from sodium (5.85 g.) in ethanol (150 c.c.)] under nitrogen. The solution was stirred at 70° during the rapid addition of 2 : 3-dibromopropyl acetate (33 g.), and was then heated on the steam-bath under reflux; it became neutral in 15 min., and after 2 hr. it was cooled, filtered from sodium bromide, and concentrated under reduced pressure. Ether and water were added to the residue, and the ethereal layer was dried and evaporated to an oil (27 g.) (Found : Ac, 1.6%); almost complete deacetylation had evidently occurred. It was fractionated at 195—215° (bath)/0.0008 mm.,  $n_D^{25}$  1.6021—1.6090. The lower-boiling fractions partly crystallised, and on trituration with methanol gave dibenzyl disulphide, m. p. and mixed m. p. 69—70°. A portion (4.9 g.) of the higher-boiling material was dissolved in dry methanol containing a trace of sodium methoxide and set aside overnight to complete the deacetylation; the product on distillation gave a main fraction (3.3 g.) of a bisbenzylthiopropyl-2-ol, b. p. 220—225° (bath)/0.0008 mm.,  $n_D^{25}$  1.6057 (Found : C, 67.0; H, 6.9; S, 21.4. Calc. for  $C_{17}H_{20}OS_2$  : C, 67.1; H, 6.6; S, 21.05%). Reacetylation with acetic anhydride and sodium acetate gave a bisbenzylthiopropyl acetate, b. p. 220—225° (bath)/0.0001 mm.,  $n_D^{25}$  1.5811 (Found : C, 66.0; H, 6.7; S, 18.3. Calc. for  $C_{19}H_{22}O_2S_2$  : C, 65.9; H, 6.4; S, 18.5%). The bisbenzylthiopropyl-2-ol gave an  $\alpha$ -naphthylurethane which after recrystallisation from benzene-petroleum (b. p. 60—80°) had m. p. 85—86°, not depressed by the authentic derivative of 1 : 3-bisbenzylthiopropyl-2-ol, but depressed to 68—76° by the 1 : 2-isomer.

*Proof of structure.* The above bisbenzylthiopropyl-2-ol (9 g.) in liquid ammonia (250 c.c.) containing ethanol (10 c.c.) was treated with sodium, added in small pieces, with stirring, until a permanent blue colour was obtained (6.5 g.). The product, isolated as described for the 1 : 2-compound, on distillation gave the dithiol (3.1 g., 82%), b. p. 75—77°/1.8 mm.,  $n_D^{25}$  1.5638 (purity by iodine titration, 96%). A portion (1.0 g.) of this was desulphurised with a suspension of Raney nickel (ca. 10 g.) in boiling water (20 c.c.) under reflux for 2 hr. The solution was filtered and distilled during the addition of a solution of sodium dichromate (1 g.) in 4N-sulphuric acid (10 c.c.); 20 c.c. of distillate were collected. A portion (1 c.c.) gave a weakly positive test for an aldehyde with Schiff's reagent. The remainder of the distillate was treated with aqueous 2 : 4-dinitrophenylhydrazine sulphate, and gave acetone 2 : 4-dinitrophenylhydrazone (0.24 g.), m. p. and mixed m. p. 124—126°.

*Reaction of 2 : 3-Dibromopropanol with Toluene- $\omega$ -thiol.*—Interaction of 2 : 3-dibromopropanol (8.6 g.), toluene- $\omega$ -thiol (10 g.), sodium (1.85 g.), and ethanol (40 c.c.) for 2 hr. under reflux, followed by working-up as described above, gave an oil (12.7 g.), b. p. 205—220°/0.0001 mm.,  $n_D^{25}$  1.6085—1.6107, consisting essentially of 1 : 3-bisbenzylthiopropyl-2-ol; it readily gave the  $\alpha$ -naphthylurethane, m. p. and mixed m. p. 84—86°.

*2 : 3-Bisbenzylsulphonylpropanol.*—30% Hydrogen peroxide (2 c.c.) was added to a solution of 2 : 3-bisbenzylthiopropyl-2-ol (0.65 g.) in acetic acid (2.5 c.c.); the mixture became hot. After 5 min., more peroxide (1 c.c.) was added, and the solution was heated on the steam-bath for 30 min., then cooled and diluted with water. The solid was collected and washed with water; recrystallisation from ethanol gave the *disulphone* (0.6 g.) as small needles, m. p. 171° (Found : C, 55.7; H, 5.8; S, 17.4.  $C_{17}H_{20}O_5S_2$  requires C, 55.4; H, 5.5; S, 17.4%). Omission of the heating on the steam-bath (compare the 1 : 3-isomer, below) gave an oily product which could not be purified.

*1 : 3-Bisbenzylsulphinylpropan-2-ol.*—30% Hydrogen peroxide (2 c.c.) was added to a solution of 1 : 3-bisbenzylthiopropyl-2-ol (0.55 g.) in acetic acid (2 c.c.). The mixture, which became very hot, was set aside for 5 min. and then poured into water. The precipitate (0.6 g.) was washed and recrystallised from a small volume of ethanol, giving the *disulphoxide* as microcrystals, m. p. 212° (Found : C, 60.3; H, 6.2; S, 19.2.  $C_{17}H_{20}O_3S_2$  requires C, 60.7; H, 6.0; S, 19.05%). Infrared absorption : see p. 1304.

*1 : 3-Bisbenzylsulphonylpropan-2-ol.*—The preceding experiment was repeated, but the reaction mixture was treated with a further quantity (1 c.c.) of 30% hydrogen peroxide and

heated on the steam-bath for 35 min. Some solid had then appeared, and more was precipitated on cooling and dilution with water. Part of the crude product (total yield, 0.6 g.) was recrystallised from acetic acid, forming short needles, m. p. 210° (Found: C, 55.5; H, 5.6; S, 17.4. Calc. for  $C_{17}H_{20}O_5S_2$ : C, 55.4; H, 5.5; S, 17.4%), and the remainder was recrystallised from a large volume of ethanol forming shining plates, m. p. 210° (Found: C, 55.3; H, 5.7%). A mixed m. p. with the disulphoxide was 208—209°. The disulphone, unlike the disulphoxide, is only very sparingly soluble in boiling ethanol. Infrared absorption: see p. 1304.

**2:3-Bisbenzylthiopropyl 2:3:4:6-Tetra-O-acetyl- $\beta$ -D-glucoside.**—A solution of 2:3-dibromopropyl 2:3:4:6-tetra-O-acetyl- $\beta$ -D-glucoside (15 g.) (Fischer, *Z. physiol. Chem.*, 1920, 108, 3) and toluene- $\omega$ -thiol (15 g.) in ethanolic sodium ethoxide [from sodium (2.75 g.) and ethanol (65 c.c.)] was stirred and boiled under reflux for 6 hr. under nitrogen. The precipitated sodium bromide (4.5 g.) was filtered off, and the filtrate was boiled for a further 2 hr., but no more solid separated. It was neutralised with carbon dioxide, concentrated under reduced pressure, and then diluted with water. The emulsion was extracted successively with (i) petroleum (b. p. 60—80°), which removed unchanged toluene- $\omega$ -thiol (6 g.); (ii) 1:1 benzene-petroleum, which removed some dibenzyl disulphide; and (iii) benzene, which gave a pale brown glass (6.6 g.). The last substance was partly purified by precipitation, as an oil, from benzene solution by addition of ether; it was dried at 100°/0.0001 mm. (Found: C, 55.6; H, 5.9; S, 12.0; Ac, 0.0%), and reacylated by treatment of a portion (2.6 g.) with acetic anhydride (15 c.c.) and sodium acetate (2 g.) for 3 hr. at 100°. Concentration under reduced pressure, addition of water, neutralisation with sodium hydrogen carbonate, and extraction with ether gave an oil (3.5 g.) which was dissolved in hot ethanol (7 c.c.). The oil which separated from the cooled solution was subjected to two further reprecipitations from ethanol, and was finally dried at 100°/0.001 mm. to give 2:3-bisbenzylthiopropyl 2:3:4:6-tetra-O-acetyl- $\beta$ -D-glucoside (2.95 g.) as a pale yellow oil,  $n_D^{25}$  1.5360 (Found: C, 58.1; H, 6.3; S, 9.4; Ac, 28.1.  $C_{31}H_{38}O_{10}S_2$  requires C, 58.7; H, 6.0; S, 10.1; Ac, 27.6%).

**Deacetylation and debenzylation.** The above product (1.5 g.) in methanolic sodium methoxide (0.2 g. of sodium in 20 c.c. of methanol) was set aside overnight. The solvent was then removed under reduced pressure and the residue was treated with water and benzene. Evaporation of the benzene extract gave the deacetylated glucoside as a pale yellow glass (0.6 g.), which was dissolved in ethanol (1.5 c.c.) and liquid ammonia (ca. 30 c.c.). Sodium (1.2 g.) was gradually added, in small pieces, to the stirred solution, until a permanent blue colour was produced. The ammonia was then boiled off, and the residue was dissolved in ethanol and 2*N*-hydrochloric acid and titrated with iodine (Found: thiol-S, calc. as free dimercaptopropyl glucoside, 11.8. Calc. for  $C_{23}H_{30}O_6S_2$ : thiol-S, 13.8%).

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