same $R_F$ value in acetone–water, another solvent system was used for separation. The content of these fractions (390 mg.) was dissolved in butan-1-ol–acetic acid–water (4 : 1 : 1 v/v, 30 ml.); after 2 days, (±)-inositol (120 mg.) had separated. After two crystallisations from water–ethanol the product was acetylated, to yield the hexa-acetate, m. p. and mixed m. p. 110°.

The mother-liquors from the isolation of (±)-inositol were run through a cellulose-powder column (9 × 1¼ in.) in butan-1-ol–acetic acid–water (4 : 1 : 1); separation of *cis*- and *epi*-inositol was not complete but from the appropriate fractions *cis*-inositol (70 mg.) was obtained by crystallisation from water–ethanol. Acetylation and crystallisation from ethanol–water gave cis*inositol hexa-acetate*, m. p. 208° (Found : C, 49·95; H, 5·45. $C_{18}H_{24}O_{12}$ requires C, 50·0; H, 5·6%). Hydrolysis with boiling ethanol containing 5% of hydrogen chloride gave cis*inositol* which was crystallised from water–ethanol (Found : C, 40·3; H, 6·9. $C_6H_{12}O_6$ requires C, 40·0; H, 6·7%). *cis*Inositol decomposes on slow heating but its uncorrected m. p. was found to be 377° (decomp.) by placing samples on a preheated aluminium block; the corrected m. p. would be approx. 390°. The *hexabenzoate*, prepared by the method described for (±)-inositol by Fletcher and Findlay,[19] crystallised from anhydrous ethanol and melted at 252° (Found : C, 71·85; H, 4·55. $C_{48}H_{36}O_{12}$ requires C, 71·65; H, 4·5%).

The fractions containing mainly *epi*inositol were combined and evaporated, and the residue was acetylated. From a solution in aqueous ethanol, *epi*inositol acetate (11 mg.) slowly crystallised; after sublimation *in vacuo* it melted at 187° (mixed m. p. 187—188°).

myo*Inositol*. Fractions 76—250 of the preliminary separation were evaporated to give *myo*inositol (712 mg.); after one crystallisation from aqueous ethanol its m. p. was 222—224°.

*Hydrogenation of* cis*Inosose*.—*cis*Inosose (18 mg.) was hydrogenated for 3 hr. in N-hydrochloric acid with Adams catalyst (5 mg.). After removal of the platinum, the solution was evaporated in a desiccator over sodium hydroxide, and the residue was separated by chromatography on a small cellulose-powder column. The inositol fraction (3 mg.) was acetylated, and the product, recrystallised from ethanol–water, had m. p. 207—208°, undepressed by admixture of *cis*inositol acetate. The quercitol fraction was acetylated to give *cis*-quercitol penta-acetate (5 mg.), m. p. 162—163°, undepressed by a sample obtained from the hydrogenation of tetrahydroxybenzoquinone.

After a small-scale hydrogenation in water with Adams catalyst paper chromatography in butan-1-ol–acetic acid–water showed the formation of *cis*inositol accompanied by a trace of *epi*inositol.

*Reduction of* cis*Inosose with Sodium Amalgam*.—To a solution of *cis*inosose (50 mg.) in water (3 ml.), kept slightly acid by additions of N-sulphuric acid as required, sodium amalgam (1 g.) was added in several portions with shaking. When the solution no longer reduced Fehling solution, it was evaporated; acetylation of the residue gave penta-*O*-acetyl*epi*inositol which, after crystallisation from ethanol–water, had m. p. and mixed m. p. 188°.

*Hydrogenation of Tetrahydroxybenzoquinone with Raney Nickel*.—A mixture of tetrahydroxybenzoquinone (10 g.), Raney nickel W-2 [20] (2 teaspoons; *ca.* 6 g.), ethanol (100 ml.), and water (70 ml.) was hydrogenated in a steel autoclave at 120°/150 atm. for 40 min. and then at 140° for 30 min. The solution was filtered, concentrated under reduced pressure, and dried over sulphuric acid.

scyllo- *and* neo-*Inositol*. The syrupy residue (7·4 g.) was diluted with methanol and crystals (65 mg.) gradually separated. Crystallisation from water–ethanol gave a product (37 mg.), m. p. >280°; on addition of more ethanol, the mother-liquor deposited further crystals (11 mg.), m. p. 218—220°, identified as *myo*inositol. The former product was acetylated and the resulting mixture of acetates was separated by extraction with hot ethanol. The ethanol solution deposited *neo*inositol hexa-acetate (8 mg.), m. p. 254°, mixed m. p. with a pure sample (m. p. 257°) 256°. The ethanol-insoluble residue (32 mg.) was sublimed *in vacuo* to give *scyllo*inositol hexa-acetate, m. p. 295—297°, mixed m. p. with an authentic sample (m. p. 292—294°) 293—295°.

The filtrate from the *scyllo*- and *neo*-inositol was worked up by cellulose-powder chromatography as described above. After preliminary separation all the fractions—except those containing *epi*-, *cis*-, and *myo*-inositol—were rechromatographed and the products grouped into Fractions A—F (not necessarily identical with the fractions carrying the same designations in the previous run). There was some overlapping of fractions : only those which appeared to show a single spot on the chromatogram were worked up.

Fraction A ($R_F$ 0·77, 700 mg.) deposited crystals (125 mg.) contaminated by oil, when stored in ethanol–ethyl acetate at 0°. Recrystallisation to constant m. p. from ethanol–ethyl acetate gave all-*cis*-*cyclo*hexane-1 : 2 : 3-triol [21] (39 mg.), m. p. and mixed m. p. 146—147° (Found : C, 54·6; H, 9·1. Calc. for $C_6H_{12}O_3$: C, 54·55; H, 9·15%). The hexabenzoate had m.p. and mixed m. p. 145°.

Fractions B ($R_F$ 0·61) and D ($R_F$ 0·44) gave no crystalline products.

*Fraction C* ($R_F$ 0·55, 300 mg.). Crystals (110 mg.), contaminated by oil, gradually separated. Fractional crystallisation gave three fractions: m. p. 220—235° (6 mg.), 165—170° (40 mg.), and 159—172° (8 mg.). Fractional sublimation *in vacuo* gave fractions of m. p. 135—145°, 177—187°, 197—225°, and 225—227°. No pure substance was obtained from this fraction.

cis*Quercitol*. Fraction E ($R_F$ 0·39, 850 mg.) deposited crystals (770 mg.) from water–ethanol; recrystallisation gave *cis*quercitol (670 mg.), m. p. 235—240° (decomp.); its acetate had m. p. and mixed m. p. 163°. The mother-liquors gave no Scherer test, showing the absence of *muco*inositol.

epi- *and* scyllo-*Quercitol and* allo*Inositol*. Fraction F ($R_F$ 0·33, 435 mg.) deposited crystals (180 mg.), m. p. 194—195°; several crystallisations gave *epi*quercitol (90 mg.), m. p. and mixed m. p. 208°. Acetylation gave a product which, after one crystallisation from ethanol–water, melted at 122—123° but after another crystallisation had m. p. 140°. *epi*Quercitol acetate was reported [22] to be dimorphous with m. p.s 123—124° and 142—143°.

The mother-liquors from *epi*quercitol—which gave the Scherer test, indicating the presence of *allo*inositol—were evaporated to dryness and chromatographed on a small cellulose-powder column. The fractions showing the presence of *allo*inositol contained a glass (80 mg.) which was acetylated and crystallised from ethanol–water. The first crystals (25 mg.), m. p. 188—191°, were recrystallised, to give *scyllo*quercitol acetate, m. p. and mixed m. p. 192—193°. Deacetylation yielded *scyllo*quercitol, m. p. and mixed m. p. 232°. The mother-liquors were concentrated, seeded with *allo*inositol acetate, and kept at 0°: crystals (29 mg.) slowly separated and, after one recrystallisation, had m. p. 136—139°. The substance was fractionally sublimed *in vacuo* and the last fraction, m. p. 142°, depressed the m. p. of *epi*quercitol acetate but not that of *allo*inositol acetate (m. p. 144°).

cis- *and* epi-*Inositol*. Fractions 51—70 of the preliminary separation, which contained *epi*- and *cis*-inositol, were evaporated to dryness; the residual syrup (510 mg.), on being dissolved in water–ethanol, deposited *epi*inositol (145 mg.; acetate, m. p. 186—187°). After concentration, more *epi*inositol (30 mg.; acetate, m. p. 187—188°) separated. Further concentration and inoculation caused the crystallisation of *cis*inositol (125 mg.; acetate, m. p. 205—206°).

Fractions 38—50 of the preliminary separation, which contained quercitols besides *epi*- and *cis*-inositol, were rechromatographed and the residue of the fractions containing only inositols (400 mg.) was crystallised from water–ethanol. The separated crystals (320 mg.) yielded *cis*-inositol (210 mg.; acetate, m. p. 206—207°) on recrystallisation.

All the mother-liquors of fractions 38—70 were combined and again run through the cellulose-powder column. The resulting fractions yielded (*a*) crystals (10 mg.), m. p. 183—190°, which were shown to be a mixture of *scyllo*- and *epi*-quercitol, (*b*) crude *cis*inositol (50 mg.; acetate, m. p. 198—203°), and (*c*) crude *epi*inositol (16 mg.; acetate, m. p. 165—172°). There was no evidence from paper chromatography for the presence of (±)-inositol in any fraction.

myo*Inositol*. Fractions 76—100 of the preliminary separation gave *myo*inositol (190 mg.) on evaporation. After one crystallisation it melted at 222°.

*Hydrogenation of Tetrahydroxybenzoquinone with Palladium–Carbon.*—A suspension of the quinone (10 g.) and of palladium–carbon (1 g.) in water (200 ml.) was hydrogenated at room temperature and pressure. In one hr. 0·9 mol. of hydrogen was taken up (hexahydroxybenzene crystallised) and 1·0 mol. was reached after 5 hr. Further amounts of catalyst (a total of 10 g.) were added until the rate of hydrogen uptake became negligible (110 hr.). At an intermediate stage, paper chromatography showed the presence of *cis*inosose but at the end of the reaction no reducing substance was present. The catalyst was removed and washed with aqueous ethanol; paper chromatography of the filtrate showed a high concentration of *myo*- and *cis*-inositol and weaker spots at $R_F$ 0·31 and 0·38. Evaporation under reduced pressure gave a resin (7·7 g.) which was taken up in methanol. *scyllo*Inositol (75 mg.) gradually crystallised; it was shown to be free from *neo*inositol by paper chromatography in phenol–water (4 : 1 w/w).

The solution decanted from the crystals was evaporated to dryness, the residue dissolved in water (7 ml.) and diluted with acetone (28 ml.); cellulose powder was added to absorb the precipitated oil. This mixture was then placed on top of the cellulose column and chromatographed as described above.

cis*Quercitol*. The contents of fractions 21—50 were run through the column again and the fractions containing *cis*-quercitol were evaporated; the residue (120 mg.) gave *cis*quercitol (40 mg.) on crystallisation from water–ethanol. The acetate had m. p. 162°, mixed m. p. 163°.

cis- *and* (±)-*Inositol.* Nearly all the *cis*inositol was in fractions 51—150; their semi-crystalline residue (3·9 g.) deposited *cis*inositol from water–ethanol, which was chromatographically pure after one recrystallisation (1·24 g.).

The mother-liquors were rechromatographed through the cellulose column, and the effluent was divided into three fractions. The first contained mainly *cis*inositol which crystallised from water–ethanol as needles (415 mg.). The mother-liquors yielded crystals (12 mg.), shown by chromatography to be those of (±)-inositol; its acetate had m. p. 105—107°. The second fraction slowly deposited crystals which were fractionally crystallised to yield pure *cis*inositol (440 mg.; acetate, m. p. 205—206°) and a mixture (160 mg.) of *cis*- and *epi*-inositol. The third fraction contained mainly *myo*inositol which was obtained pure (m. p. 224°, 420 mg.) by one crystallisation from water-ethanol.

scyllo*Quercitol and* epi*inositol.* All the mother-liquors and solid material remaining after the isolation of *cis*- and *myo*-inositol were combined and run through a cellulose column. The first product to emerge was acetylated and crystallised from ethanol, to yield *scyllo*quercitol acetate (10 mg.), m. p. and mixed m. p. 192°. The second half of the fractions containing *cis*- and *epi*-inositol was evaporated, and the residue acetylated, and crystallised from ethanol–water, to give *epi*inositol acetate (65 mg.), m. p. and mixed m. p. 187—188°. Considerable amount of *cis*inositol was still left in mother-liquors.

scyllo- *and* myo-*Inositol.* The contents (570 mg.) of fractions 181—260 were fractionally crystallised from water–ethanol: *scyllo*inositol (24 mg.) separated first. The remainder was combined with fractions 151—180, to yield *myo*inositol (360 mg.), m. p. 221—222°.

*Hydrogenation of Tetrahydroxybenzoquinone with Palladium–Carbon at High Pressure.*—The quinone (10 g.) in water (150 ml.) was hydrogenated with palladium–carbon for 2 hr.: 1·1 l. of hydrogen were absorbed and hexahydroxybenzene was precipitated. The mixture was transferred to a steel autoclave, more catalyst (10 g.) and water (100 ml.) were added, and the suspension was stirred under a hydrogen pressure of 100 atm. After 23 hr. the reduction was still incomplete; the mixture was further hydrogenated at 45—50° for 19 hr. after which no reducing compounds were present. The catalyst was removed and the filtrate was evaporated to dryness. The crude material (8·4 g.) was redissolved in a little water, leaving *scyllo*inositol (250 mg.) undissolved.

*Absorption on ion-exchange resin.* The filtrate was diluted to 300 ml. with water and was shaken for 20 min. with a strong base anion-exchange resin (Deacidite FF; 200 g.), converted into the borate form according to the directions of Lock and Richards.[14] Paper chromatography of the solution showed that all *cis*inositol had been removed but some *myo*- and *scyllo*-inositol and unidentified material remained. The solution was filtered; the filtrate (containing 1·8 g. of material) was not worked up.

To remove the weakly bound cyclitols, the resin was shaken with water (300 ml.) for 1 hr.; the filtrate contained *myo*inositol. This process was repeated twenty times but even in the last washing *myo*inositol could still be detected. The combined washings were evaporated and the residue was repeatedly distilled with methanol until no more methyl borate was formed. The residue (1·3 g.) was found, by paper chromatography, to consist mainly of *myo*inositol but to contain another compound having $R_F$ 0·44. To isolate the latter the residue was chromatographed on a cellulose column; the fractions showing a spot at $R_F$ 0·44 gave a gum (135 mg.) on evaporation which, after acetylation, deposited crystals (50 mg.) from ethanol–water. Several recrystallisations gave a *quercitol penta-acetate*, m. p. 115—117° (Found: C, 51·5; H, 6·0. $C_{16}H_{22}O_{10}$ requires C, 51·35; H, 5·9%). After deacetylation, the quercitol decomposed at 230—240° without melting. It is not identical with any of the known quercitols.

*Desorption from the resin.* The resin was shaken twice with N-hydrochloric acid (400 ml.); the filtrates were evaporated, and boric acid was removed by distillation with methanol. Crystallisation from water–ethanol gave, first, *scyllo*inositol (55 mg.), then a crop of *cis*inositol (850 mg.). The mother-liquors were found to contain *cis*- and *epi*(or *scyllo*)-quercitol, *cis*-, *epi*-, and *myo*-inositol. By cellulose-powder chromatography *cis*quercitol (460 mg.) and *cis*inositol (340 mg.) were isolated; other fractions and mother-liquors, which contained more *cis*inositol, were not worked up.

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