501. *Synthesis of 2-O-Methyl- and 3 : 4-Di-O-methyl-D-galacturonic Acid.**

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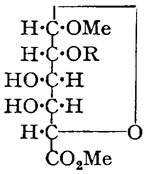
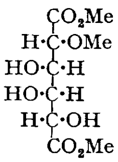
Crystalline methyl (methyl 3 : 4-*O*-*iso*propylidene-α-D-galactosid)uronate (B) has been synthesised from D-galactose. Methylation of (B) gave methyl (methyl 2-*O*-methyl-3 : 4-*O*-*iso*propylidene-α-D-galactosid)uronate (C) which was characterised by isolation of a crystalline amide, by oxidation to dimethyl 2-*O*-methyl-D-galactarate and by formation of the known crystalline diamide thereof. Hydrolysis of (C) gave 2-*O*-methylgalacturonic acid which on appropriate treatment gave the same diamide.

The crystalline 2-toluene-*p*-sulphonyl derivative of (B) was prepared, and removal of the *iso*propylidene residue followed by methylation and reductive fission of the toluene-*p*-sulphonyl group gave methyl 3 : 4-di-*O*-methyl-D-galactosiduronic acid. The methyl ester and its corresponding amide and methylamide were also obtained.

Apart from their intrinsic interest the methyl ethers of galacturonic acid are of great importance in the structural studies of the polysaccharides occurring in plant gums and pectins and in certain bacterial polysaccharides. Methylation followed by hydrolysis of these polysaccharides has led to a number of partially methylated galacturonic acid derivatives (Luckett and Smith, *J.*, 1940, 1106, 1506; Hirst, Hough, and Jones, *J.*, 1949, 3145; Brown, Hirst, and Jones, *J.*, 1949, 1761; Hough and Jones, *J.*, 1950, 1199). In addition G. A. Adams *et al.* (*Canad. J. Res.*, 1950, **28**, *B*, 753; *Canad. J. Chem.*, 1951, **29**, 109) isolated a monomethyl galacturonic acid from the hydrolysis products of the unmethylated polysaccharide from the hemicelluloses of wheat. The present work is concerned with the synthesis of 2-*O*-methyl- and 3 : 4-di-*O*-methyl-galacturonic acid. Methyl (methyl 2-*O*-methyl-α-D-galactopyranosid)uronate (I; R = Me) has been synthesised previously by Jones and Stacey (*J.*, 1947, 1340) from 1 : 2 : 3 : 4-tetra-*O*-acetyl-6-*O*-tritylgalactose, which on removal of the trityl residue and oxidation gave 1 : 2 : 3 : 4-tetra-*O*-acetylgalacturonic acid. Hydrolysis of the acetyl groups and treatment with 1% methanolic hydrogen chloride then gave methyl (methyl α-D-galactosid)uronate (I; R = H). The hydroxyl groups at $C_{(3)}$ and $C_{(4)}$ were blocked by an *iso*propylidene residue and methylation followed by hydrolysis gave methyl (methyl 2-*O*-methyl-D-galactosid)uronate in approximately 7·5% overall yield. The present synthesis differs in the earlier stages and gives a 20% overall yield. 1 : 2-3 : 4-Di-*O*-*iso*propylidene-D-galactose was oxidised with permanganate, giving crystalline potassium 1 : 2-3 : 4-di-*O*-*iso*propylidene-D-galacturonate monohydrate. This was converted into the crystalline free acid monohydrate which when boiled in dry methanol with cation-exchange resins furnished crystalline methyl (methyl α-D-galactosid)uronate. Although different conditions for the substitution and for the removal of the *iso*propylidene residue have been used, the subsequent stages were the same as those employed by Jones and Stacey (*loc. cit.*). In the present experiments the syrupy methyl (methyl 2-*O*-methyl-3 : 4-*O*-*iso*propylidene-α-D-galactopyranosid)uronate was characterised by the isolation of a crystalline amide and by oxidation to dimethyl 2-*O*-methylgalactarate (II). This, on appropriate treatment, gave the known crystalline diamide. Hydrolysis of the *iso*propylidene and glycosidic and



(I)



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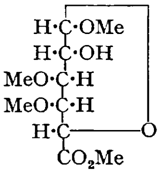

(III)

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* For nomenclature, see *J.*, 1952, 5108, especially rules 9, 20, 26, 27, and 28.

ester methoxyl groups from methyl (methyl 2-*O*-methyl-3 : 4-*O*-*iso*propylidene-α-D-galactopyranosid)uronate and oxidation of the resulting 2-*O*-methyl-D-galacturonic acid with bromine water gave the same dimethyl ester which after treatment with methanolic ammonia furnished the above-mentioned crystalline diamide.

Crystalline methyl (methyl 3 : 4-di-*O*-methyl-α-D-galactopyranosid)uronate (III) has been synthesised by blocking position 2 in crystalline methyl (methyl 3 : 4-*O*-*iso*propylidenegalactosid)uronate with a toluene-*p*-sulphonyl group. Hydrolysis of the *iso*propylidene residue followed by methylation gave crystalline methyl (methyl 3 : 4-di-*O*-methyl-2-*O*-toluene-*p*-sulphonylgalactosid)uronate. Reductive fission of the toluene-*p*-sulphonyl group with sodium amalgam and separation from the toluenesulphinic acid and metallic ions by adsorption on ion-exchange resins followed by preferential elution led to the isolation of crystalline methyl 3 : 4-di-*O*-methylgalactosiduronic acid. Treatment with methanolic hydrogen chloride furnished the methyl ester (III) as long needles, and appropriate treatment gave a crystalline amide and methylamide. It was converted into crystalline methyl (methyl-2 : 3 : 4-tri-*O*-methyl-α-D-galactopyranosid)uronate. Hydrolysis of (III) followed by oxidation gave crystalline diethyl 3 : 4-di-*O*-methylgalactarate. The corresponding crystalline dimethyl ester and diamide were isolated.

EXPERIMENTAL

Methyl (Methyl α-D-Galactopyranosid)uronate.—D-Galactose (80·0 g.) was converted into 1 : 2-3 : 4-di-*O*-*iso*propylidene-D-galactose by the method described by Ohle and Berend (*Ber.*, 1925, **58**, 2585). The syrupy product, when distilled in a high vacuum, had b. p. 130—170°/0·03 mm., n_D^{25} 1·4657 (yield, 55·3 g., 76%), $[\alpha]_D^{19}$ $-51°$ (*c*, 1·2 in H_2O) [Found: $COMe_2$, 44·9. Calc. for $C_{12}H_{20}O_6$: $COMe_2$, 44·6%).

Oxidation of this syrup (55·0 g.) by potassium permanganate as described by Ohle and Berend (*loc. cit.*) gave potassium 1 : 2-3 : 4-di-*O*-*iso*propylidene-D-galacturonate monohydrate (48 g., 70%), m. p. 200° (decomp.), $[\alpha]_D^{21}$ $-70°$ (*c*, 2·0 in H_2O) (Found: C, 43·3; H, 5·5; $COMe_2$, 36·0. Calc. for $C_{12}H_{17}O_7K,H_2O$: C, 43·6; H, 5·8; $COMe_2$, 35·2%). 1 : 2-3 : 4-Di-*O*-*iso*propylidene-D-galacturonic acid was obtained by treatment of this (16 g.) with cation-exchange resins (Amberlite I.R. 100-H) (24 g.) in distilled water (200 c.c.) for 6 hr. The resins were removed by filtration and the filtrate was passed through a column (250 × 18 mm.) of the same resin. Removal of part of the water gave the acid as colourless crystals (12·7 g., 91%), m. p. 158°, $[\alpha]_D^{17}$ $-79°$ (*c*, 0·9 in $CHCl_3$) (Niemann and Link, *J. Biol. Chem.*, 1934, **104**, 197, record m. p. 157°, $[\alpha]_D$ $-84°$) (Found: C, 50·1; H, 6·9; $COMe_2$, 40·0; CO_2, 16·1. Calc. for $C_{12}H_{18}O_7,H_2O$: C, 49·3; H, 6·9; $COMe_2$, 39·8; CO_2, 15·1%).

1 : 2-3 : 4-Di-*O*-*iso*propylidene-D-galacturonic acid monohydrate (13·9 g.) was boiled for 24 hr. with dry methanol (200 c.c.) containing cation-exchange resins (Amberlite I.R. 100-H). Removal of the resins and evaporation gave a colourless syrup which on trituration with ethanol partly crystallised (3·6 g., 32%). Repeated treatment of the mother-liquor with methanol and resins brought the total yield of crystalline methyl (methyl α-D-galactosid)uronate to 7·48 g. (66%), m. p. 145°, $[\alpha]_D^{16}$ $+121°$ (*c*, 1·0 in H_2O) (Jones and Stacey, *loc. cit.*, record m. p. 147°, and Niemann and Link, *loc. cit.*, $[\alpha]_D$ $+121°$) (Found: C, 39·9; H, 6·6; OMe, 26·5. Calc. for $C_8H_{14}O_7,H_2O$: C, 40·0; H, 6·7; OMe, 25·8%).

*Methyl (Methyl 3 : 4-*O-iso*Propylidene-α-D-galactosid)uronate.*—Methyl (methyl α-D-galactosid)uronate monohydrate (3·6 g.) was shaken for 120 hr. with dry acetone (250 c.c.) containing acetaldehyde (2 drops) and anhydrous copper sulphate (30 g.). A white solid was obtained which on recrystallisation from light petroleum (b. p. 60—80°) gave colourless needles (3·62 g., 94%), m. p. 113—114°, $[\alpha]_D$ $+117°$ (*c*, 1·2 in H_2O) (Jones and Stacey, *loc. cit.*, record m. p. 107°, $[\alpha]_D^{20}$ $+118°$) (Found: C, 50·8; H, 6·7; OMe, 23·2. Calc. for $C_{11}H_{18}O_7$: C, 50·4; H, 6·9; Me, 23·7%).

*Methyl (Methyl 2-*O*-Methyl-α-D-galactopyranosid)uronate.*—The foregoing *iso*propylidene compound (3·8 g.) was methylated thrice with methyl iodide and silver oxide, and the product distilled (b. p. 120—130°/0·1 mm.) as a colourless syrup (*A*) (2·70 g., 72%), n_D^{17} 1·4622, $[\alpha]_D^{16}$ $+103°$ (*c*, 0·7 in H_2O), $+114°$ (*c*, 0·8 in MeOH) (Found: C, 52·8; H, 7·4; OMe, 33·3. Calc. for $C_{12}H_{20}O_7$: C, 52·2; H, 7·3; OMe, 33·7%). This was characterised by conversion into the crystalline *amide* by treatment with methanolic ammonia. After recrystallisation from ethanol–light petroleum (b. p. 60—80°) the crystals had m. p. 123—124°, $[\alpha]_D^{19}$ $+70°$ (*c*, 1·1 in H_2O)

(Found : C, 49·9; H, 7·1; N, 5·0; OMe, 23·7. $C_{11}H_{19}O_6N$ requires C, 50·6; H, 7·3; N, 5·4; OMe, 23·8%).

Mild hydrolysis of the *iso*propylidene residue was carried out in three ways : (1) A solution of the syrup (*A*) (2·48 g.) in methanol (50 c.c.) containing water (0·20 c.c.) was shaken with dry cation-exchange resins (Amberlite I.R. 100-H) (1·5 g.) for 6 days. Filtration and removal of the solvent gave methyl (methyl 2-*O*-methyl-α-D-galactopyranosid)uronate as a colourless syrup (2·18 g., 98%), n_D^{17} 1·4680, $[\alpha]_D$ +105° (*c*, 0·7 in MeOH), +113° (*c*, 0·8 in H_2O) (Jones and Stacey, *loc. cit.*, record n_D 1·4732, $[\alpha]_D^{20}$ +80°) (Found : C, 45·3; H, 6·9; OMe, 39·7. Calc. for $C_9H_{16}O_7$: C, 45·8; H, 6·8; OMe, 39·4%). (2) Similar treatment of (*A*) for 48 hr. at 50° gave a syrup (98%), $[\alpha]_D$ +97° (*c*, 0·7 in MeOH). (3) Treatment of (*A*) with 0·5% methanolic hydrogen chloride at 70° for 70 min. gave a syrup (98%), n_D^{17} 1·4679, $[\alpha]_D^{17}$ +4·0° (*c*, 1·7 in H_2O) (Brown, Hirst, and Jones, *J.*, 1949, 1761, record $[\alpha]_D$ +21° in H_2O). The derived amide, after recrystallisation from ethanol–ether, had m. p. 174—175°, $[\alpha]_D^{15}$ +60° (*c*, 1·3 in H_2O) (Jones and Stacey, *loc. cit.*, record m. p. 174°, $[\alpha]_D^{18}$ +55° in EtOH) (Found : C, 43·8; H, 6·6; N, 6·8; OMe, 28·4. Calc. for $C_8H_{15}O_6N$: C, 43·4; H, 6·8; N, 6·3; OMe, 28·1%).

Characterisation of Methyl (*Methyl* 2-O-*Methyl*-3 : 4-O-iso*propylidene- and* 2-O-*Methyl*-α-D-*galactosid*)*uronate*.—A portion of the syrup (*A*) (0·12 g.) was oxidised with nitric acid (*d* 1·3) by raising the temperature from 40° to 80° during 15 min., and then kept at 80° for 10 min. After removal of the nitric acid by distillation under diminished pressure, with frequent additions of water, the product was esterified by boiling it for 6 hr. with methanolic hydrogen chloride (4%). The resulting ester, dimethyl 2-*O*-methyl-D-galactarate, gave on distillation a syrup (0·07 g.), b. p. 160—180°/0·1 mm., from which a crystalline diamide, m. p. 205° (decomp.), was obtained on treatment with methanolic ammonia for 48 hr. at 0° (Jones and Stacey, *loc. cit.*, record m. p. 200°; Brown, Hirst, and Jones, *loc. cit.*, give m. p. 195° for this product from methylated *Cholla* gum; Hough and Jones, *loc. cit.*, give m. p. 207° for the same derivative from methylated gum from *Sterculia setigera*).

The syrup (*A*) (0·3 g.) was hydrolysed with 0·2N-sulphuric acid at 100° until the rotation was constant ($[\alpha]_D$ +36°; 48 hr.). Neutralisation was effected with barium carbonate and 2-*O*-methyl-D-galacturonic acid was obtained as a colourless syrup ($[\alpha]_D^{18}$ +42°), after elution through a column (160 × 12 mm.) of cation-exchange resin (Amberlite I.R. 120-H). Oxidation with bromine, followed by ester formation, furnished dimethyl 2-*O*-methyl-D-galactarate which had n_D^{15} 1·4640, $[\alpha]_D^{18}$ +34° (*c*, 3·0 in H_2O). The diamide prepared as above had m. p. 205° (decomp.) (Found : C, 37·8; H, 6·2; N, 11·6; OMe, 14·9. Calc. for $C_7H_{14}O_6N_2$: C, 37·8; H, 6·4; N, 12·6; OMe, 14·0%).

Methyl (*Methyl* 3 : 4-O-iso*Propylidene*-2-O-*toluene*-p-*sulphonyl*-α-D-*galactosid*)*uronate*.—The above-mentioned *iso*propylidene derivative, m. p. 113—114° (0·931 g.), was dissolved in dry pyridine (20 c.c.) and kept with "Drierite" (12 g.) at 0° for 20 hr. Toluene-*p*-sulphonyl chloride (1·6 g.) in dry pyridine (10 c.c.) was added in small portions during several hours, the mixture being kept at 0°. The solution was then set aside for 24 hr. at 0°, for 24 hr. at 15°, and for 72 hr. at 30° (unless these conditions are observed the yield is much diminished). The mixture was cooled to 0°, the "Drierite" removed by filtration, and water (100 c.c.) cautiously added with constant cooling. *Methyl* (*methyl* 3 : 4-O-iso*propylidene*-2-O-*toluene*-p-*sulphonyl*-α-D-*galactosid*)*uronate* (*B*) was deposited as colourless needles (1·02 g.), m. p. 157—158°, $[\alpha]_D^{20}$ +122° (*c*, 1·1 in MeOH), +117° (*c*, 2·2 in $CHCl_3$) (Found : C, 52·0; H, 5·5; S, 8·1; OMe, 14·6. $C_{18}H_{24}O_9S$ requires C, 51·9; H, 5·8; S, 7·8; OMe, 14·9%). After removal of the crystals, extraction of the aqueous filtrate with chloroform and removal of the solvent gave a further yield (0·23 g.) of crystals (total yield, 1·255 g., 85%).

Methyl (*Methyl* 3 : 4-*Di*-O-*methyl*-2-O-*toluene*-p-*sulphonyl*-α-D-*galactosid*)*uronate*.—The crystals (*B*) (1·345 g.), dissolved in 1% methanolic hydrogen chloride (130 c.c.), were kept at 30° for 30 hr. After neutralisation with silver carbonate *methyl* (*methyl* 2-O-*toluene*-p-*sulphonyl*-α-D-*galactosid*)*uronate* (*C*) (1·18 g., 97%) was obtained. After recrystallisation from aqueous methanol it had m. p. 71°, $[\alpha]_D^{18}$ +61° (*c*, 1·1 in $CHCl_3$) (Found : C, 45·8; H, 5·7; S, 8·4; OMe, 15·2. $C_{15}H_{20}O_9S,H_2O$ requires C, 45·7; H, 5·6; S, 8·1; OMe, 15·7%). Methanolic anhydrous ammonia quantitatively converted the ester into the *amide* which crystallised on removal of the solvent. The amide after recrystallisation from methanol had m. p. 94—95°, $[\alpha]_D^{18}$ +67° (*c*, 0·5 in $CHCl_3$) (Found : C, 45·1; H, 5·6; N, 3·5; S, 8·1; OMe, 8·2. $C_{14}H_{19}O_8NS,H_2O$ requires C, 44·3; H, 5·6; N, 3·7; S, 8·4; OMe, 8·2%).

The product (*C*) (1·18 g.) was methylated four times with methyl iodide and silver oxide. The resultant *dimethyl ether* (1·21 g., 96%) was dissolved in warm ethanol and crystallisation induced by the addition of water. After recrystallisation from aqueous methanol it had m. p.

83°, n_D^{20} 1·4900, $[\alpha]_D^{17}$ +82° (*c*, 1·1 in $CHCl_3$), +88° (*c*, 2·4 in EtOH) (Found: C, 50·2; H, 5·8; OMe, 29·5; S, 8·1. $C_{17}H_{24}O_9S$ requires C, 50·5; H, 6·0; OMe, 30·7; S, 7·9%).

Methyl 3 : 4-*Di*-O-*methyl*-α-D-*galactosiduronic Acid.*—Anion-exchange resin (Amberlite I.R.A. 400-OH) was packed into four short glass tubes (60 × 10 mm.) which were arranged alternately with three similar tubes containing cation-exchange resin (Amberlite I.R. 120-H) to form a column, and the whole washed with distilled water (300 c.c.), with ethanol (200 c.c.), and with methanol (200 c.c.).

Methyl (methyl 3 : 4-di-*O*-methyl-2-*O*-toluene-*p*-sulphonyl-α-D-galactosid)uronate (1·2 g.), dissolved in methanol (20 c.c.), was stirred at room temperature with 0·25N-aqueous sodium hydroxide (12 c.c.) during 30 min.; thereafter sodium amalgam (4%; 15 g.) was added during 6 hr. with continuous stirring. The mixture was stirred for a further 18 hr. and then the solids were removed by filtration and washed with methanol. After treatment with solid carbon dioxide the combined filtrates were evaporated to dryness and a white solid was obtained which was repeatedly extracted with dry methanol under reflux. The cooled methanolic extracts (200 c.c.) were passed through a column, prepared as described above, 3—4 c.c. of eluate being collected during a minute, and, after complete elution, the eluate was recycled through the column which was finally washed with methanol (100 c.c.). Removal of the solvent from the combined eluate and washings gave a syrup (0·03 g.) which was discarded. The column was dismantled and the portions containing the anion-exchange resin reassembled and eluted by slow passage (60 hr.) of 2% formic acid in methanol (500 c.c.). Removal of solvent from the eluate, under reduced pressure, gave *methyl* 3 : 4-*di*-O-*methyl*-α-D-*galactosiduronic acid* as a colourless syrup (0·613 g., 87%) which crystallised spontaneously. Recrystallised from ethanol–light petroleum (b. p. 60—80°) it had m. p. 154—155°, $[\alpha]_D^{15}$ +158° (*c*, 1·3 in $CHCl_3$), +156° (*c*, 1·3 in MeOH), +163° (*c*, 1·3 in H_2O) (Found: C, 46·4; H, 7·0; OMe, 38·4. $C_9H_{16}O_7$ requires C, 45·8; H, 6·8; OMe, 39·4%).

Methyl (*Methyl* 3 : 4-*Di*-O-*methyl*-α-D-*galactosid*)*uronate.*—Methyl 3 : 4-di-*O*-methyl-α-D-galactosiduronic acid (0·375 g.), dissolved in methanolic hydrogen chloride (1%; 32 c.c.), was kept at 30° for 48 hr. The solution was neutralised with silver carbonate, and the filtrate after evaporation to dryness at 40°/15 mm. furnished a crystalline ester. Recrystallisation from light petroleum (b. p. 60—80°) gave needles of *methyl* (*methyl* 3 : 4-*di*-O-*methyl*-α-D-*galactosid*)-*uronate* (0·378 g., 95%), m. p. 113—114°, $[\alpha]_D^{16}$ +165° (*c*, 0·4 in $CHCl_3$) (Found: C, 48·0; H, 7·1; OMe, 49·8. $C_{10}H_{18}O_7$ requires C, 48·0; H, 7·25; OMe, 49·6%). The crystalline amide and *methylamide* were prepared by treating the ester, in the usual manner, with methanolic ammonia, and with methanolic methylamine respectively. The amide, after trituration with ethanol, had m. p. 130—131°, $[\alpha]_D^{17}$ +108° (*c*, 1·1 in EtOH). The methylamide, obtained as prisms on recrystallisation from acetone, had m. p. 205°, $[\alpha]_D^{15}$ +116° (*c*, 0·6 in H_2O) (Found: C, 48·5; H, 7·5; N, 5·8; OMe, 38·8. $C_{10}H_{19}O_6N$ requires C, 48·2; H, 7·7; N, 5·6; OMe, 37·4%).

The ester (0·018 g.) was methylated twice with methyl iodide and silver oxide, and crystalline methyl (methyl 2 : 3 : 4-tri-*O*-methyl-α-D-galactopyranosid)uronate (0·019 g.) was obtained. It had m. p. 71—72° (after sublimation *in vacuo*) alone and admixed with an authentic specimen.

Diethyl 3 : 4-*Di*-O-*methylgalactarate.*—The foregoing dimethyl ether ester (0·294 g.) was hydrolysed at 100° with sulphuric acid (20 c.c., 0·2N), the rotations observed being $[\alpha]_D$ +160° (0 hr.), +118° (3·5 hr.), +112° (6·5 hr.), +100° (24 hr.), +90° (31 hr.), +84° (48 hr., const.). The solution was neutralised with barium carbonate and filtered through a well-washed bed of charcoal–"Filter Cel," and barium ions were removed by passage of the filtrate through a column (300 × 10 mm.) of Amberlite (I.R. 120-H) ion-exchange resin. The clear eluate was concentrated to a colourless syrup, n_D^{11} 1·4615, $[\alpha]_D^{16}$ +37° (*c*, 1·2 in EtOH), +93° (*c*, 1·3 in H_2O). The syrup (0·22 g.) in water (15 c.c.) was oxidised with bromine (2 c.c.) at 40°, the rotations observed being $[\alpha]_D$ +93° (0 hr.), 80° (1 day), 60° (3 days), 23° (5 days), 15° (8 days, constant). After removal of the water and hydrobromic acid under diminished pressure with frequent addition of ethanol the syrupy residue was heated in hydrochloric acid (10 c.c.; 0·2N) at 100° for 50 hr. by which time the rotation had fallen to +8°. Further treatment with bromine (2 c.c.) for 3 days at 40° gave a solution with $[\alpha]_D$ ±0°. Removal of the water and hydrobromic acid as above gave crystalline *diethyl* 3 : 4-*di*-O-*methylgalactarate*. Recrystallisation from aqueous acetone gave flat plates, m. p. 148—149°, $[\alpha]_D$ ±0° [Found: C, 49·4; H, 7·4; OR (as OMe), 42·2. $C_{12}H_{22}O_8$ requires C, 49·0; H, 7·5; OR (as OMe), 42·2%]. Treatment with methanolic hydrogen chloride (1·5%) at 60° for 16 hr. gave a crystalline product. Recrystallisation from acetone–light petroleum (b. p. 60—80°) furnished *dimethyl* 3 : 4-*di*-O-*methylgalactarate* as needles, m. p. 172—173°, $[\alpha]_D$ ±0° (Found: 44·8; H, 6·7. $C_{10}H_{18}O_8$ requires

C, 45·1; H, 6·8%). The derived *diamide*, after recrystallisation from methanol, had m. p. 230° (decomp.), $[\alpha]_D$ ±0° (Found: N, 11·9. $C_8H_{16}O_6N_2$ requires N, 11·9%).

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