563. *The Cross-linking of Cellulose and its Derivatives. Part III.*[1] *The Addition of Amines to Crotonyl Esters.*

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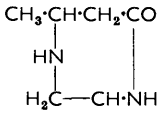
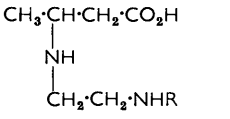
The addition of some primary aliphatic amines to ethyl crotonate and 1,2:5,6-di-*O*-isopropylidene-D-glucose 3-crotonate, and of this sugar ester to amino-derivatives of simple sugars, has been investigated; the products have been identified as far as possible.

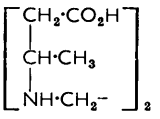
THE general purport of this work has been previously described,[1] stress being laid on the possible value of addition of amines to crotonyl esters of cellulose in the formation and estimation of cross-links. Although this reaction has already been used to induce insolubility in cellulose crotonates,[2] the process of cross-linking has been inferred to occur by β-addition of a diamine to the double bonds without formal corroboration. From the work of Stadnikow [3] and Morsch [4] it is known that crotonates add the elements of ammonia and simple amines to form β-amino- and β-alkylamino-butyrates as well as the corresponding amides, the relative contributions of addition and aminolysis depending on the conditions. The object of the present work, therefore, has been to determine the validity of applying this reaction to carbohydrate derivatives and to establish, for analytical purposes, the structures of the cross-links formed between molecules.



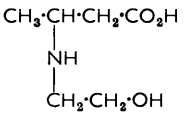
(I)



(II; R = H) (III; R = Ac)



(IV)



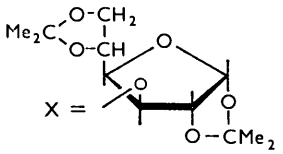
(V)

We first studied the reaction between methyl crotonate and ethylenediamine. At temperatures significantly above 20° aminolysis leads to a complex mixture from which β-*N*-2′-aminoethylaminobutyric lactam (I) was isolated; this was hydrolysed by hydrochloric acid to the acid (II), which was isolated as the crystalline dihydrochloride. This compound is more satisfactorily obtained by addition of *N*-acetylethylenediamine to ethyl crotonate at lower temperatures and subsequent saponification of the product (III). The product (IV) of diaddition, being crystalline, is readily isolated from the low-temperature reaction between ethylenediamine and ethyl crotonate.

The addition to 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose 3-crotonate (VI) was next examined. Ethanolamine had been found to add to crotonic acid *via* the ammonium salt to form the acid (V), and with the sugar crotonate it gave a product that on hydrolysis

[1] Part I, Corbett and McKay, *J. Soc. Dyers and Colourists*, in the press; Part II, preceding paper.
[2] Engelmann and Exner, *Makromol. Chem.*, 1957, **23**, 233.
[3] Stadnikow, *Ber.*, 1911, **44**, 52; *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 900; 1910, **42**, 885.
[4] Morsch, *Monatsh.*, 1932, **60**, 50.

yielded 1,2:5,6-di-*O*-isopropylidene-D-glucose (VII) and the same acid (V). The addition compound can thus be represented as the aminobutyrate (VIII). There is no addition of ethanolamine or ammonia to the 3-but-2′-enyl or 3-allyl ether of di-*O*-isopropylidene-D-glucose. The 3-acetate is also not attacked by ethanolamine during 18 hr. at room



(VI) X·CO·CH:CHMe

(VII) XH

(VIII) X·CO·CH$_2$·CHMe·NH·CH$_2$·CH$_2$·OH

(IX) X·CH$_2$·CH$_2$·NH$_2$

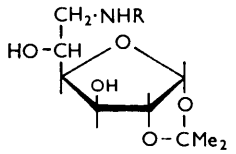
X·CH$_2$·CH$_2$·NH·CHMe·CH$_2$·CO·X (X)

X·CH$_2$·CH$_2$·CH$_2$·NH$_2$ (XI)

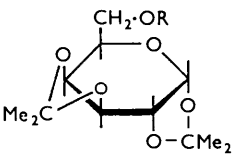
temperature, suggesting that little aminolysis of unsubstituted crotonyl groups occurs and that addition is to the sugar ester and not to liberated crotonamide. Reaction between the sugar crotonate (VI) and ethylenediamine yields the addition product (XV), since it gives on hydrolysis the glucofuranose derivative (VII) and the diacid (IV).

We then studied a case where the amine was itself a sugar derivative. 6-Amino-6-deoxy-1,2-*O*-isopropylidene-D-glucofuranose (XII) was treated with the sugar crotonate (VI) and from the products a component was isolated whose analyses corresponded to those of the disugar compound (XIII). Hydrolysis of this yielded the component sugar (VII) and the carbohydrate amino-acid derivative (XIV).

Reaction of 3-*O*-2′-aminoethyl-1,2:5,6-di-*O*-isopropylidene-D-glucose (IX) with the sugar crotonate (VI) gave a product with an analysis corresponding to the adduct (X), but because of the small amount available, the only crystalline material which could be isolated after hydrolysis was the component (VII). The same behaviour was observed



X as above



(XII) R = H

(XIII) R = CHMe·CH$_2$·CO·X

(XIV) R = CHMe·CH$_2$·CO$_2$H

X·CO·CH$_2$·CHMe·NH·CH$_2$·CH$_2$·NH·CHMe·CH$_2$·CO·X (XV)

(XVI) R = CH$_2$·CH$_2$·NH$_2$

(XVII) R = CH$_2$·CH$_2$·CH$_2$·NH$_2$

(XVIII) R = CH$_2$·CH$_2$·NH·CHMe·CH$_2$·CO$_2$H

(XIX) R = CH$_2$·CH$_2$·CH$_2$·NH·CHMe·CH$_2$·CO$_2$H

with the more readily available 3-*O*-3′-aminopropyl derivative (XI). When the amines (XVI) and (XVII) reacted with the crotonate (VI), not only did the products give correct analyses for the addition compounds but on hydrolysis they yielded, in addition to the component (VII), crystalline compounds corresponding in analysis to the acid components (XVIII) and (XIX),

It is evident that these three types of reaction are capable of forming bridges between pairs of carbohydrate molecules. It is true that the glucose and galactose derivatives used cannot be regarded as exactly analogous to the substituted glucoses in cellulose derivatives. Nevertheless, the addition occurs readily in the face of considerable steric opposition by the isopropylidene substituents and should not be greatly hindered when applied to cellulosic systems.

Experimental

Addition of Ethylenediamine to Methyl Crotonate at 65°.—To a refluxing solution of ethylenediamine (60 g.) in methanol (200 ml.) in an atmosphere of nitrogen methyl crotonate (100 g.) in methanol (100 ml.) was added dropwise, during 5 hr. Refluxing was continued for a further 24 hr., and then the solvent was removed by distillation to leave a colourless syrup. Repeated sublimation of the syrup, or exhaustive extraction with benzene followed by recrystallisation of

the extract from ethyl acetate containing a little methanol, gave colourless needles of β-2′-*aminoethylaminobutyric lactam* (I) (17 g., 13%), m. p. 113—114° (Found: C, 56·6; H, 9·2; N, 21·6. $C_6H_{12}N_2O$ requires C, 56·2; H, 9·4; N, 21·9%), that gave a *picrate*, m. p. 242° (Found: C, 40·4; H, 4·3; N, 19·6. $C_{12}H_{15}N_5O_8$ requires C, 40·4; H, 4·2; N, 19·6%), and an *acetate*, needles, m. p. 100—101° (Found: C, 56·8; H, 8·3; N, 16·2. $C_8H_{14}N_2O_2$ requires C, 56·6; H, 8·3; N, 16·4%).

A solution of the lactam (2 g.) in 10% hydrochloric acid (35 ml.) was refluxed for 4 hr. and then concentrated. Recrystallisation of the residue from ethanol–ether gave needles of β-2′-*aminoethylaminobutyric acid dihydrochloride* (as II) (2 g.), m. p. 150—151° (Found: C, 32·8; H, 7·4; Cl, 33·7; N, 12·8. $C_6H_{16}Cl_2N_2O_2$ requires C, 32·9; H, 7·3; Cl, 32·7; N, 12·8%). This was converted into the syrupy free amine by treatment with Amberlite IR-4B (OH) resin. Esterification with ethanolic hydrogen chloride gave the *ester dihydrochloride*, m. p. 111° (from benzene–ethanol), and showing evidence of hydration in the infrared spectrum (Found: C, 38·1; H, 8·0; Cl, 27·8. $C_8H_{20}Cl_2N_2O_2,\frac{1}{2}H_2O$ requires C, 37·7; H, 8·2; Cl, 27·7%).

Addition of Ethylenediamine to Ethyl Crotonate at 4°.—A solution of ethyl crotonate (30 g.) and ethylenediamine (8 g.) in ethanol (100 ml.) was kept at 4° for 5·5 days. Ethanol and unchanged amine were removed by evaporation and the residue heated with water for 2 hr. Concentration of the solution gave a syrup which gave crystals from ethanol–ether. After one recrystallisation from aqueous ethanol the NN′-*ethylenedi*-(β-*aminobutyric acid*) (IV) (5·5 g., 18%) had m. p. 216—218° (Found: C, 51·5; H, 8·5; N, 12·2. $C_{10}H_{20}N_2O_4$ requires C, 51·8; H, 8·6; N, 12·1%), that gave a *dipicrate*, m. p. 205—206° (Found: C, 38·2; H, 3·8; N, 16·2. $C_{20}H_{26}N_8O_{18}$ requires C, 38·2; H, 3·8; N, 16·2%), a dark blue *copper salt* (Found: C, 40·9; H, 6·5; Cu, 21·1; N, 9·2. $C_{10}H_{18}CuN_2O_4$ requires C, 40·9; H, 6·2; Cu, 21·7; N, 9·6%), and a *diethyl ester dihydrochloride*, m. p. 194—195° (Found: C, 46·8; H, 8·4; N, 7·8. $C_{14}H_{30}Cl_2N_2O_4$ requires C, 46·5; H, 8·3; N, 7·8%).

Addition of N-*Acetylethylenediamine to Ethyl Crotonate at* 4°.—A solution of mono-*N*-acetylethylenediamine [5] (18·5 g.) and ethyl crotonate (18·5 g.) in ethanol (70 ml.) was kept at 4° for 6 days. A small amount of solid, m. p. 293° (decomp.), which separated was removed and the solution concentrated to retain the components of b. p. >80°. This residue was dissolved in water and extracted with ether to remove unchanged ethyl crotonate (2—3 g.). The aqueous phase was evaporated to a syrup which yielded microcrystals from ethanol–ether. After two recrystallisations β-2′-*acetylamidoethylaminobutyric acid* (III) (17·5 g., 55%) had m. p. 158—160° (Found: C, 51·0; H, 8·5; N, 14·7. $C_8H_{16}N_2O_3$ requires C, 51·1; H, 8·5; N, 14·9%).

The acetyl derivative (2 g.) was treated for 3 hr. with 5% boiling aqueous potassium hydroxide (100 ml.), then the solution was neutralised with carbon dioxide and evaporated. The residue was extracted with ethanol and the extract evaporated to dryness, treated with hydrochloric acid, and evaporated again. This residue was also extracted with alcohol. Addition of chloroform to this extract gave colourless crystals of β-2′-*aminoethylaminobutyric acid dihydrochloride*. After two recrystallisations from ethanol–acetone, the salt (0·9 g., 39%) had m. p. 151—152° (Found: C, 32·6; H, 7·6; N, 12·4. $C_6H_{16}Cl_2N_2O_2$ requires C, 32·9; H, 7·3; N, 12·8%). Addition of ether to the mother-liquors yielded crystals; after three recrystallisations from ethanol–ether the *ethyl* β-2′-*aminoethylaminobutyrate dihydrochloride* (1·4 g., 40%) had m. p. 111—112° (Found: C, 37·8; H, 8·2; N, 11·1. $C_8H_{20}Cl_2N_2O_2,\frac{1}{2}H_2O$ requires C, 37·7; H, 8·2; N, 10·9%).

Addition of Ethanolamine to Crotonic Acid.—To a solution of crotonic acid (4 g.) in ethanol (50 ml.) was added ethanolamine (3 ml.). After 18 hr. at room temperature the solution was concentrated to give white crystals, m. p. 88—91°. Recrystallisation from acetone–light petroleum (b. p. 40—60°) afforded 2-*hydroxyethylammonium crotonate* (4·6 g., 69%), m. p. 85—90° (Found: C, 49·0; H, 9·0; N, 9·5. $C_6H_{13}NO_3$ requires C, 49·0; H, 8·9; N, 9·5%).

The salt took up 4·80, 4·85, 5·35, and 5·88 moles of oxygen in $\frac{1}{4}$, $\frac{1}{2}$, 1, and 5 hr., respectively, when oxidised with acidic permanganate at 23°. On long standing, or on heating at 100° for 1 hr., the salt reverted to a pale brown syrup which, after extraction with acetone, left a residue. This recrystallised from ethanol–light petroleum (b. p. 40—60°) to give β-2′-*hydroxyethylaminobutyric acid* (V), m. p. 181·5—183·5° (Found: C, 49·4; H, 9·1; N, 9·6. $C_6H_{13}NO_3$ requires C, 49·0; H, 8·9; N, 9·5%).

In contrast *ethylenediammonium crotonate*, m. p. 121·5—122·5°, is stable on storage and at 100° (Found: C, 51·8; H, 8·8; N, 12·0. $C_{10}H_{20}N_2O_4$ requires C, 51·8; H, 8·6; N, 12·1%).

[5] Hill and Aspinall, *J. Amer. Chem. Soc.*, 1939, **61**, 822.

1,2:5,6-*Di*-O-*isopropylidene*-D-*glucofuranose* 3-*Crotonate* (VI) (with Mr. J. A. D. EWART).—The crotonate is obtained by treating the sodium salt of di-*O*-isopropylidene-D-glucofuranose with crotonyl chloride, or di-*O*-isopropylidene-D-glucopyranose with crotonic anhydride and pyridine. The *crotonate* product was best purified by distillation under a high vacuum and then readily crystallised, having m. p. 65·5—67°, $[\alpha]_D^{22}$ −48·4° (*c* 4·7 in chloroform) (Found: C, 58·5; H, 7·4; OCr, 21·2. $C_{16}H_{24}O_7$ requires C, 58·5; H, 7·4; OCr, 21·0%).

3-O-*But*-2′-*enyl*-1,2:5,6-*di*-O-*isopropylidene*-D-*glucofuranose*.—The di-*O*-isopropylidene-D-glucofuranose (1·0 g.), powdered sodium hydroxide (0·4 g.), and dioxan (5 ml.) were stirred at 45° whilst but-2-enyl bromide (4 ml.) was added during 20 min. The mixture was heated with stirring for 1½ hr. at 50°, and then 3 hr. at 55—60°. Water was added, and the mixture extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and concentrated to a liquid (1·2 g., 104%) which distilled at 120°/0·02 mm. (bath-temp.). The *ether* had n_D^{21} 1·4602, and $[\alpha]_D^{20}$ −18·8° (*c* 1·3 in chloroform) (Found: C, 61·1; H, 8·4. $C_{16}H_{26}O_6$ requires C, 61·2; H, 8·4%).

3-O-*Allyl*-1,2:5,6-*di*-O-*isopropylidene*-D-*glucofuranose*.—The *allyl ether* was prepared similarly to the butenyl ether and had b. p. 113°/0·005 mm. (bath-temp.), n_D^{24} 1·4570, $[\alpha]_D^{20}$ −12·7° (*c* 2·4 in chloroform) (Found: C, 59·5; H, 8·1. $C_{15}H_{24}O_6$ requires C, 60·0; H, 8·1%).

Addition of Ethanolamine to 1,2:5,6-*Di*-O-*isopropylidene*-D-*glucofuranose* 3-*Crotonate*.—To the ester (3·691 g.) in ether (75 ml.) was added ethanolamine (0·675 ml.). The whole was kept at room temperature for 70 hr., then concentrated under reduced pressure to a syrup (4·458 g., 102%), that in a short-path still volatilised at 140°/0·005 mm. It was 1,2:5,6-*di*-O-*isopropylidene*-D-*glucofuranose* (β-2′-*hydroxyethylaminobutyrate*) (VIII) (Found: C, 55·5; H, 8·3; N, 3·0. $C_{18}H_{31}NO_8$ requires C, 55·6; H, 8·1; N, 3·6%).

This ester (0·397 g.) was kept in pyridine (10 ml.) with toluene-*p*-sulphonyl chloride (0·43 g.) at room temperature for 22 hr., then poured into ice-water and treated in the usual manner to give, as a syrup, 1,2:5,6-*di*-O-*isopropylidene*-D-*glucofuranose* 3-(β-2′-*toluene*-p-*sulphonyloxyethylaminobutyrate*) *toluene*-p-*sulphonate* (Found: C, 53·6; H, 6·3; S, 8·8. $C_{32}H_{45}NO_{13}S_2$ requires C, 53·7; H, 6·3; S, 9·0%).

The ester (VIII) (0·717 g.) slowly crystallised. Extraction with hot light petroleum (b. p. 60—80°) then left a residue (0·251 g., 92%), which after recrystallisation from acetone–alcohol had m. p. 178—180°, undepressed upon admixture with β-2′-hydroxyethylaminobutyric acid (V). Concentration of the light petroleum liquors afforded di-*O*-isopropylidene-D-glucose, m. p. 111—112°, in theoretical yield. This hydrolysis was accelerated by addition of water.

Addition of Ethylenediamine to 1,2:5,6-*Di*-O-*isopropylidene*-D-*glucofuranose* 3-*Crotonate*.—A solution of the crotonate (3·155 g.) and ethylenediamine (0·32 ml.) in ethanol (75 ml.) was kept at room temperature for 2¾ days before being concentrated under reduced pressure to a straw-coloured syrup (3·802 g., 102%). A sample (0·860 g.) was distilled to give fractions (*a*) (0·390 g.), b. p. 110—120°/0·01 mm. (bath-temp.), m. p. 105° (impure di-*O*-isopropylidene-D-glucose), and (*b*) (0·258 g.), b. p. 155—170°/0·01 mm. (bath-temp.), n_D^{20} 1·4680. The latter was *bis*-(1,2:5,6-*di*-O-*isopropylidene*-D-*glucofuranose*) 3,3′-[NN′-*ethylenedi*-(β-*aminobutyrate*)] (XV) and underwent autohydrolysis on storage (Found: 56·9; H, 8·1; N, 3·0. $C_{34}H_{56}N_2O_{14}$ requires C, 57·0; H, 7·9; N, 3·9%).

The ester (2·939 g.) and water (50 ml.) were heated together for 3 hr. at 75—80°, and the resulting solution concentrated under reduced pressure to give a partly crystalline syrup (2·814 g.). This was extracted with light petroleum (4 × 50 ml.; b. p. 60—80°), concentration of the extracts giving di-*O*-isopropylidene-D-glucose (1·372 g., 72%). The residue was further extracted with acetone (50 ml.), concentration of the extract giving a syrup (0·659 g., 24%) which crystallised to give more di-*O*-isopropylidene-D-glucose, m. p. 105—108·5°. The hygroscopic residue was digested with hot ethanol, affording the crystalline acid (IV) (0·180 g., 21%) which after two recrystallisations from water–ethanol–acetone had m. p. 217·5—218·5° (Found: C, 51·5; H, 8·4; N, 11·7. Calc. for $C_{10}H_{20}N_2O_4$: C, 51·8; H, 8·6; N, 12·1%).

Addition of 6-*Amino*-6-*deoxy*-1,2-O-*isopropylidene*-D-*glucofuranose to* 1,2:5,6-*Di*-O-*isopropylidene*-D-*glucofuranose* 3-*Crotonate*.—A solution of the amino-sugar (0·137 g.) and the crotonate (0·206 g.) in ethanol (10 ml.) was kept at room temperature for 8½ days, the optical rotation falling from $[\alpha]_D$ −28·5° to −18·1°. The solution was concentrated to a syrup, and ether was added, giving an amorphous unidentified product (0·130 g.). Concentration of the mother-liquors gave a syrup (0·269 g.) which in a short-path still at 170°/0·005 mm. gave the *amino-ester* (XIII) (Found: C, 54·5; H, 7·6; N, 2·3. $C_{25}H_{41}NO_{12}$ requires C, 54·9; H, 7·6; N, 2·6%).

The syrup partly crystallised during several months and was then extracted with hot light petroleum (b. p. 60—80°) to give impure di-*O*-isopropylidene-D-glucose, m. p. 100—102°.

The crude syrup (XIII) (5·586 g.) was stirred for 5 hr. at room temperature with water (80 ml.); crystals (1·926 g.) that separated recrystallised from ethanol, giving di-*O*-isopropylidene-D-glucose 3-crotonate, m. p. 66—67·5°. Concentration of the aqueous solution gave a syrup (3·660 g.) which was extracted with hot light petroleum (b. p. 40—60°). The residue (3·413 g.) crystallised from ethanol–ether to give material (0·623 g.) of m. p. 208—209·5°; several recrystallisations of this afforded 6-(2-*carboxy*-1-*methylethylamino*)-6-*deoxy*-1,2-O-*isopropylidene*-D-*glucofuranose* (XIV), m. p. 187—189° (C, 51·0; H, 7·7; N, 4·2. $C_{13}H_{23}NO_7$ requires C, 51·2; H, 7·6; N, 4·6%).

Addition of 3-O-2′-*Aminoethyl*-1,2:5,6-*di*-O-*isopropylidene*-D-*glucofuranose to* 1,2:5,6-*Di*-O-*isopropylidene*-D-*glucofuranose* 3-*Crotonate*.—A solution of the amine (0·387 g.) and the ester (0·420 g.) in ethanol (25 ml.) was kept at room temperature for 18 hr. before being concentrated to a syrup. Distillation of the residue gave fractions (*a*) b. p. 140°/0·005 (bath-temp.), n_D^{22} 1·4689, which slowly crystallised to give 1,2:5,6-di-*O*-isopropylidene-D-glucose 3-crotonate, m. p. 55—56°, and (*b*) b. p. 175°/0·005 mm., n_D^{23} 1·4680. The latter was the *ether-ester* (X) (0·253 g.) (Found: C, 57·2; H, 7·7; N, 1·9. $C_{30}H_{49}NO_{13}$ requires C, 57·1; H, 7·8; N, 2·2%). This (0·097 g.) was digested with hot water for 1 hr., and the resulting solution concentrated to a syrup (0·052 g.), that distilled (short-path) at 120°/0·01 mm. The volatile residue (0·045 g.) partly crystallised (0·012 g.) on trituration with ether. Concentration of the ethereal mother-liquors gave a syrup which sublimed at 100°/15 mm. to give white needles, m. p. 100—104°, of di-*O*-isopropylidene-D-glucose.

Addition of 6-O-2′-*Aminoethyl*-1,2:3,4-*di*-O-*isopropylidene*-D-*galactopyranose to* 1,2:5,6-*Di*-O-*isopropylidene*-D-*glucofuranose* 3-*Crotonate*.—A solution of the amine (0·853 g.) and the crotonate (0·919 g.) in ethanol (50 ml.) was kept at room temperature for 18 hr. before being concentrated at 40° to a syrup. Fractional distillation of the syrup gave fractions (*a*) (0·464 g.), b. p. 130—140°/0·005 mm. (bath-temp.) (Found: C, 56·7; H, 7·7%), (*b*) (0·418 g.), b. p. 135—150°/0·005 mm. (bath-temp.) (Found: C, 57·7; H, 7·9%), and (*c*) (0·296 g.), b. p. 175—190°/0·005 mm. (bath-temp.), n_D^{23} 1·4700, $[\alpha]_D^{20}$ −68·6° (*c* 0·79 in chloroform). The last was the 1,2:5,6-*di*-O-*isopropylidene*-D-*glucose* 3-*ester* of the galactose derivative (XVIII) (Found: C, 56·9; H, 7·8; N, 2·3. $C_{30}H_{49}NO_{13}$ requires C, 57·1; H, 7·8; N, 2·2%).

This addition compound (0·825 g.) was suspended in water (50 ml.) at room temperature for 4 days. The insoluble residue (0·211 g.) was unhydrolysed compound. Concentration of the aqueous solution gave a syrup (0·548 g.) which was extracted with light petroleum (3 × 20 ml.; b. p. 60—80°). The residue (0·077 g.) was crystallised several times from ethanol–ether–light petroleum (b. p. 40—60°) to give 6-O-[2-N-(2-*carboxy*-1-*methylethyl*)*aminoethyl*]-1,2:3,4-*di*-O-*isopropylidene*-D-*galactopyranose* (XVIII), m. p. 156—157·5°, $\nu_{max.}$ 1600 cm.$^{-1}$ (ionised amino-acid) (Found: N, 3·9; $C_{18}H_{31}NO_8$ requires N, 3·6%).

Addition of 3-O-3′-*Aminopropyl*-1,2:5,6-*di*-O-*isopropylidene*-D-*glucofuranose to* 1,2:5,6-*Di*-O-*isopropylidene*-D-*glucofuranose* 3-*Crotonate*.—A solution of the amine (2·990 g.) and the crotonate (3·10 g.) in ethanol (200 ml.) was kept at room temperature for 2 days and then concentrated at 40°. The syrup (2·087 g.) was distilled to give fractions (*a*) b. p. 135°/0·005 mm. (bath-temp.) (which crystallised to give di-*O*-isopropylidene-D-glucose, m. p. and mixed m. p. 111·5—113°), (*b*) b. p. 160—165°/0·005 mm., n_D^{18} 1·4677, $[\alpha]_D$ −35·0° (*c* 2 in chloroform) (Found: C, 57·9; H, 8·1; N, 1·1%), and (*c*) (0·477 g.) b. p. 165°/0·005 mm. (bath-temp.), n_D^{18} 1·4670, $[\alpha]_D$ −21·2° (*c* 2 in chloroform). The last was the 3-*ester* of 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose and 3-*O*-[3-*N*-(2-carboxy-1-methylethyl)aminopropyl]-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (Found: C, 57·9; H, 8·3; N, 2·1. $C_{31}H_{51}NO_{13}$ requires C, 57·7; H, 8·0; N, 2·2%).

Autohydrolysis of an aqueous suspension of the addition product gave a syrup from which only di-*O*-isopropylidene-D-glucose was isolated.

Addition of 6-O-3′-*Aminopropyl*-1,2:3,4-*di*-O-*isopropylidene*-D-*galactopyranose to* 1,2:5,6-*Di*-O-*isopropylidene*-D-*glucofuranose* 3-*Crotonate*.—A solution of the amine (4·996 g.) and the crotonate (5·106 g.) in ethanol (200 ml.) was kept at room temperature for 18 hr. and then concentrated at 40° to a syrup, n_D^{23} 1·4650, $[\alpha]_D^{22}$ −57·4° (*c* 1·0 in chloroform). A sample was distilled to give 1,2:5,6-*di*-O-*isopropylidene*-D-*glucose* 3-*ester*, n_D^{23} 1·4670, $[\alpha]_D^{23}$ −60·8° (*c* 1·0 in chloroform), b. p. 135°/0·005 mm. (bath-temp.), of the acid (XIX) (Found: C, 57·3; H, 7·7; N, 1·9. $C_{31}H_{51}NO_{13}$ requires C, 57·7; H, 8·0; N, 2·2%).

The undistilled reaction product (3·664 g.) was triturated with water (15 ml.) and then kept

at room temperature for 3 days. The aqueous layer was decanted from the residue (0·870 g.) and concentrated under reduced pressure to a syrup (2·440 g.) which was extracted with light petroleum (b. p. 60—80°) to leave material (0·995 g.), m. p. 176·5—178°. Several recrystallisations from light petroleum (b. p. 60—80°) gave the 6-O-[3-N-(2-*carboxy*-1-*methylethyl*)*amino*-*propyl*]-1,2:3,4-*di*-O-*isopropylidene*-D-*galactopyranose* (XIX), m. p. 190—191·5°, $[\alpha]_D^{23}$ −64·0° (*c* 1·0 in chloroform) (Found: C, 56·4; H, 8·1; N, 3·6. $C_{19}H_{33}NO_8$ requires C, 56·5; H, 8·3; N, 3·5%). The petroleum extract gave di-*O*-isopropylidene-D-glucose (1·390 g.), m. p. 111—112°.

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