NOTES.

507. *Ditellurium Decafluoride.*

By W. D. English and J. W. Dale.

The lower fluorides of tellurium are not well known, and there is doubt as to the existence of many of the reported compounds (see, *e.g.*, Sidgwick, " The Chemical Elements and Their Compounds," Vol. II, Oxford Univ. Press, 1950, pp. 990, 991). Yost and Claussen (*J. Amer. Chem. Soc.*, 1933, **55**, 885) reported that a by-product from the direct fluorination of tellurium had a higher molecular weight (340) than tellurium hexafluoride (242). They did not obtain enough to investigate it adequately, but Yost and Russell (" Systematic Inorganic Chemistry," Prentice-Hall Inc., New York, 1944, pp. 295, 299) later stated that the compound was probably impure ditellurium decafluoride.*

We have obtained ditellurium decafluoride in yields of up to 20% from the direct fluorination of tellurium in the presence of calcium fluoride. This compound was similar to disulphur decafluoride (Denbigh and Whytlaw-Gray, *J.*, 1934, 1346) in most of its properties such as odour, toxicity, and chemical behaviour.

Ditellurium decafluoride is a colourless, heavy liquid of remarkable volatility. Though

---

* Since this paper was submitted, the existence of tellurium tetrafluoride has been confirmed by Junkins, Bernhardt, and Barber (*J. Amer. Chem. Soc.*, 1952, **74**, 5749).

it has a molecular weight of 445 it boils at 327° K, by far the highest ratio of molecular weight to boiling point of any compound known. Its physical properties are:

M. p. −34° to −33°. V. p. equation (−33° to 54°) : $\log p_{\text{mm.}} = -2063/T + 9{\cdot}20$ (r.m.s. deviations : ±1°). B. p. : calc., 54°; obs., 53°/748 mm. Heat of evaporation at normal b. p. (calc.) : 9440 cal./mole. Trouton constant : 28·8 cal. mole^{-1} deg.$^{-1}$.* n_D^{20} 1·298; $d_{25}^{25} = 2{\cdot}88$.

Ditellurium decafluoride is fairly stable and may be stored for several months without much decomposition. However, it slowly attacks glass. The vapour attacks organic stop-cock greases immediately, turning them black, and the liquid dissolves fluorinated stop-cock greases. It reacts with acetone, turning it brown, and releases iodine from acetone solutions of potassium iodide, as does sulphur decafluoride.

Distilled water, or 1, 5, or 20% aqueous sodium hydroxide, had no apparent effect on liquid ditellurium decafluoride during 18 hours. Sodium attacked the compound slowly and quietly; potassium reacted with it vigorously and with frequent small explosions; both reactions yielded an insoluble black powder (Te?).

The yield was affected by conditions as follows. (i) Dilution of the fluorine with nitrogen reduced the yield. (ii) Dilution of the tellurium with sodium fluoride instead of calcium fluoride prevented the production of ditellurium decafluoride. (iii) Increase in the ratio of calcium fluoride to tellurium from 4·5 : 1 to 6·25 : 1 increased the yield by one-fifth.

Experimental.—Apparatus. The apparatus in which the fluorination took place consisted of a pile of three copper trays, 9 × 25 cm., with hollow bottoms through which cold water circulated. The trays were enclosed in a copper box, 10 × 26 × 16 cm. Fluorine was introduced by means of a perforated ring over each tray. Products were removed from the end of the box by a manifold and were condensed in Pyrex traps cooled in liquid air.

Synthetic procedure. Tellurium (100 g., of particle size such that 90% passed a 250-mesh and 65% a 325-mesh sieve) was mixed with calcium fluoride (450 g.; 50% passing a 100-mesh sieve), and the mixture dried at 110° for 2 days. It was then placed in the trays. The cooling water was turned on and fluorine was passed through at 16 g./hr. The reaction was continued until large quantities of unchanged fluorine started to condense in the trap cooled in liquid air. Distillation of the product yielded 117 g. (62%) of tellurium hexafluoride, 25 g. (19%) of *ditellurium decafluoride* (Found : Te, 56·9; F, 42·5. Te_2F_{10} requires Te, 57·3; F, 42·7%), and 0·5 ml. of an unidentified yellow oil, b. p. 92°/480 mm. The decafluoride had a molecular weight of 450 by vapour density (Calc. : 445) and MR_D 28·7 (Calc. : 27·6, AR_D for tellurium being taken as 8·80, see Fajans and Joos, *Z. Physik*, 1924, **33**, 27).

Ditellurium decafluoride was not produced when sodium fluoride (of particle size as for tellurium, above) was used to dilute the tellurium.

The authors thank Mr. B. MacCrone for technical assistance, and the Superintendent of Defence Research Chemical Laboratories for permission to publish this work. This paper is published as D.R.C.L. No. 92.

DEFENCE RESEARCH CHEMICAL LABORATORIES,
OTTAWA, CANADA.

[PRESENT ADDRESS OF W. D. E.:
PENNSYLVANIA STATE COLLEGE, PA., U.S.A.]

[*Received, September 20th,* 1952.]

---

* Disulphur decafluoride has a Trouton constant of 23·0 (Denbigh and Whytlaw-Gray, *loc. cit.*) or, more probably, 20·2 (Hoffman, personal communication).

508. cyclo*Octatetraene Derivatives. Part II.* Condensation of* cyclo*Octatetraene with Phenol.*

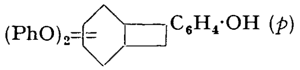
By WILLIAM O. JONES.

THE reaction between *cyclo*octatetraene and phenol has been examined; concentrated hydrochloric acid and boron trifluoride–acetic acid complex were good catalysts; stannous chloride, aluminium chloride, zinc chloride, and sulphuric acid were less effective. Phenol condensed with *cyclo*octatetraene in the molecular ratio of 3 : 1, and to ensure complete utilisation of the hydrocarbon, 4—6 mol. of phenol were used at 20—50°. Higher temperatures led to dark rubber-like products which became brittle on storage.

The normal product was a pale pink solid, melting indefinitely at 120—130°, which could not be satisfactorily crystallised even after chromatographic resolution. Distillation at 0·8 mm. appeared to cause structural changes in the product.

Methylation gave a colourless ether, m. p. 50—55°, which yielded a small amount of anisic acid on oxidation. The phenolic condensation product gave a derivative of phenoxyacetic acid by reaction with chloroacetic acid. Neither of these derivatives was sharp melting. The equivalent weight of the phenoxyacetic acid indicated that only one of the three phenol molecules had retained its hydroxyl group, the other two presumably being present as phenoxy-groups.

The phenol reacted rapidly with 8 mol. of chlorine, suggesting substitution in the phenoxy-groups (2 × 3) and the phenolic part (2). A trinitro-derivative was also made.



Because of the intractability of the phenolic condensation product and its derivatives, conclusive proof of its structure has not been obtained. To account for the present results the annexed formula is tentatively suggested as representing the type of compound produced.

o- and *p*-Chlorophenols and resorcinol have also been condensed with *cyclo*octatetraene.

Experimental.—Condensation product from cyclo*octatetraene and phenol.* *cyclo*Octatetraene (20·8 g.), phenol (113 g.), and concentrated hydrochloric acid (1 ml.) were stirred for 18 hours at room temperature, and the resulting viscous mixture was steam-distilled. The residue cooled to a pale pink brittle solid (62 g.; m. p. 125—130°). Amorphous material (Found: C, 78·1; H, 6·8%) was invariably obtained from all attempts at crystallisation. Chromatography on alumina gave only gummy products. In another experiment the product was distilled at 0·8 mm. Two fractions were collected, at 100—180° (orange) and at 180—230° (red), but the major portion could not be distilled. Both fractions melted at 25—30°, and they now formed brownish-red solutions (green fluorescence) in dilute sodium hydroxide, whereas before distillation such solutions were almost colourless.

At 70° a vigorous exothermic reaction occurred and the flask filled with a dark blue rubber-like material, which became brittle and was almost insoluble in dilute sodium hydroxide.

The condensation product (10 g.) was converted, by methyl sulphate, into its methyl ether (10 g.), m. p. 50—55°, which could not be obtained crystalline (Found: C, 79·8; H, 7·6%). The ether (5 g.) yielded anisic acid (0·5 g.; m. p. 182—184°; equiv., 160) when oxidised with potassium permanganate (20 g.) in boiling sodium carbonate solution (200 ml.; 5%).

An impure phenoxyacetic acid (m. p. 120—140°; equiv., 413) was prepared in the usual manner.

Dropwise addition of fuming nitric acid (11 g.) at 5—15° to a solution of the condensation product (19 g.) in acetic acid (200 ml.) gave a trinitro-derivative (25·5 g.). This was purified by passage of an aqueous solution of the sodium salt through alumina. The *derivative* was eventually obtained as a pale yellow powder (from chloroform), m. p. 140—150° (Found: C, 59·3; H, 4·6; N, 7·2. $C_{26}H_{23}N_3O_9$ requires C, 59·9; H, 4·4; N, 8·1%).

The rate of chlorination of the condensation product was determined at 20° by treating it (0·477 g.) with chlorine (10 mol.) in acetic acid (500 ml.) and removing samples (5 ml.) periodically for titration. 8 mol. of chlorine were absorbed in 3 min., at which point there was a sharp break in the time–titre curve.

Condensation products from cyclo*octatetraene and other phenols.* With *o*- and *p*-chlorophenol

---

* Part I, *J.*, 1953, 2036.

the reaction was carried out at 55° but for 10 hr. The crude mixtures did not thicken very much, and approximately 50% of the *cyclo*octatetraene was recovered. The *o*-isomer gave an alkali-soluble black product (m. p. 150—170°) whereas that from the *p*-isomer was dark brown (m. p. 60—70°) and was not soluble in alkali. To obtain adequate mixing, the reaction between resorcinol (270 g.) and *cyclo*octatetraene (52 g.) was carried out in acetic acid (200 ml.) at 20—28° in the presence of boron trifluoride–acetic acid (2·5 ml.). The residue obtained on steam-distillation consisted of an intense brownish-red solution, from which a solid (viscous at first, but brittle later; m. p. 165—200°; 63 g.) was obtained on acidification. The product was readily soluble in dilute sodium carbonate solution.

The author thanks the Directors of the British Oxygen Company Ltd. for permission to publish this note.

THE BRITISH OXYGEN COMPANY, LTD.,
MORDEN ROAD, LONDON, S.W.19.

[*Received, December* 13*th*, 1952.]

509. 2 : 4 : 5-*Trimethyl* D-*Arabonamide.*

By P. W. KENT and M. W. WHITEHOUSE.

IN the demonstration of the ring structure of methylfuranosides of D-glucosamine, methylation and oxidation would be expected to lead to 2 : 4 : 5-trimethyl D-arabinose. This sugar has been obtained by the action of hypochlorite on 3 : 5 : 6-trimethyl D-gluconamide (Haworth, Peat, and Whetstone, *J.*, 1938, 1975) as a syrup having properties characteristic of an *aldehydo*-sugar, *viz.*, ready reaction with potassium permanganate and Fehling's solutions, and restoration of the colour to Schiff's reagent. No crystalline derivatives were reported. A recent re-examination (Dodgson and Pryde, *Nature*, 1952, **170**, 35) of the " trimethylarabinose " obtained in this way showed it to be a mixture of at least four substances which could be separated chromatographically: one fraction only had typical aldehydic properties and this corresponded to a dimethyl pentose; another contained nitrogen.

We have now prepared 2 : 4 : 5-trimethyl D-arabinose by direct oxidation of 3 : 5 : 6-trimethyl D-glucose by sodium metaperiodate. The initial trimethyl glucose (Anderson, Charlton, and Haworth, *J.*, 1929, 1329) was chromatographically homogeneous and yielded a syrupy but homogeneous trimethyl pentose which readily reduced Fehling's solution, restored the colour to Schiff's reagent, and had an absorption band at 2550—2650 Å comparable with that of penta-acetyl *aldehydo*glucose (Wolfrom, *J. Amer. Chem. Soc.*, 1929, **51**, 2188). Further oxidation with bromine gave the corresponding arabonic acid from which an ester and thence crystalline 2 : 4 : 5-trimethyl D-arabonamide were obtained. The amide gave a negative Weerman test.

Experimental.—Chromatographic constants were determined throughout on Whatman No. 1 paper in butanol–ethanol–water (4 : 1 : 5). R_G values refer to the ratio of the distance traversed by a sugar to that of 2 : 3 : 4 : 6-tetramethyl glucose, when investigated simultaneously.

2 : 4 : 5-*Trimethyl* D-*arabinose*. 3 : 5 : 6-Trimethyl D-glucose {0·9 g.; n_D^{20} 1·4660, $[\alpha]_D^{22}$ −9° (*c*, 1·8 in H_2O), R_G 0·86} and sodium metaperiodate tetrahydrate (1·35 g.) were dissolved in water (100 ml.). Trimethyl arabinose was detected chromatographically after 6 hr. at room temperature in darkness. After 24 hr. barium carbonate (5 g.) was added and the solution was extracted with chloroform and the dried extract was concentrated to a syrup from which the product was extracted with acetone. Cautious evaporation of the solvent gave syrupy 2 : 4 : 5-trimethyl D-arabinose (0·5 g.), n_D^{17} 1·4655, $[\alpha]_D^{20}$ +18·5° (*c*, 0·6 in $COMe_2$), R_G 0·96 (Found: OMe, 46·2. $C_8H_{16}O_5$ requires OMe, 48·2%).

Methyl (2 : 4 : 5-*trimethyl* D-*arabonate*). 2 : 4 : 5-Trimethyl D-arabinose (0·105 g.) in water (5 ml.) containing bromine (8 drops) was kept for 5 days, whereafter it had no reducing properties. Excess of bromine was removed by aeration and the solution neutralised with silver carbonate. The filtrate was saturated with hydrogen sulphide, and after refiltration and evaporation the resulting acid was esterified by boiling 1% methanolic hydrogen chloride for

5 hr. The solution, neutralised with silver carbonate and filtered, gave on evaporation *methyl* (2 : 4 : 5-*trimethyl* D-*arabonate*), n_D^{17} 1·4438 (Found : OMe, 56·1. $C_9H_{18}O_6$ requires OMe, 56·1%).

2 : 4 : 5-*Trimethyl* D-*arabonamide*. The above ester, dissolved in dry saturated methanolic ammonia was kept at 0° for 24 hr. Removal of the solvent gave the *amide* which, recrystallised from acetone, had m. p. 144°, $[\alpha]_D^{21}$ $-35{\cdot}2°$ (*c*, 0·5 in EtOH), R_G 0·78 (Found : N, 6·5; OMe, 45·8. $C_8H_{17}O_5N$ requires N, 6·8; OMe, 45·0%) (cf. 2 : 3 : 5-trimethyl D-arabonamide, m. p. 137—138° $[\alpha]_D^{19}$ $-19°$ in MeOH, and 2 : 3 : 4-trimethyl D-arabonamide, m. p. 96°, $[\alpha]_D^{20}$ $-25°$ in MeOH).

DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF OXFORD. [*Received, March 30th*, 1953.]

---

510. *The System* $Cr_2(SO_4)_3$–H_2SO_4–H_2O.

By DUNCAN TAYLOR.

IN the system $Al_2(SO_4)_3$–H_2SO_4–H_2O, Taylor and Bassett (*J.*, 1952, 4431) have shown that, (*a*) as the acid concentration increases at 25° the solid phase $Al_2(SO_4)_3,16H_2O$ is followed by an unusual series of hydrated acid sulphates, (*b*) the 14-hydrate appears as a stable solid phase only at higher temperatures (50—60°), and (*c*) the anhydrous sulphate is not obtained except in concentrated acid solutions near the boiling point. In view of the well-known isomorphism of aluminium and chromic compounds, it was of interest to see if the same behaviour was observed in the corresponding chromic sulphate system, especially since in the latter there is a much stronger tendency for the formaton of complex co-ordination compounds. Furthermore, although extensive data are available regarding hydrated and acid sulphates of chromium (Mellor, " Inorganic and Theoretical Chemistry," Longmans, 1924, Vol. 11, p. 434), no systematic investigation of the ternary system appears to have been published previously.

From our work it is concluded that (*a*) chromium does not form a series of hydrated acid sulphates as does aluminium, and (*b*) many of the data in Mellor (*op. cit.*) regarding acid sulphates of chromium are unreliable.

Experimental.—Phase-equilibria data were obtained at 25° by using techniques very similar to those already described for the aluminium sulphate system, except that to obtain dry samples of the solid phases the wash liquid was methanol at low sulphuric acid concentrations and acetone containing 10% by volume of methanol at high acid concentrations. These wash-liquids caused no dissolution of the solid phases and no precipitation of solids from the appropriate saturated solutions. Several months' stirring were used in all cases to establish solid–liquid equilibrium. This was essential because it was frequently observed, particularly at low acid concentrations, that a solid phase may be precipitated but redissolved within a few days as the nature of the chromium co-ordination in the liquid phase changed.

Chromic sulphate (B.D.H.) was used as starting material without further purification; it was shown to contain slightly more than 16 molecules of water of crystallisation and had an *X*-ray powder photograph identical with that of solid A (see Table). Other reagents were " AnalaR " wherever possible.

Analytical procedure. All samples of liquid and solid phases, except the anhydrous sulphate, were analysed for total sulphate and chromium, water being determined by difference. Experiments with synthetic mixtures showed that total sulphate could be determined with an accuracy of a few parts in 1000 (low tendency rather than high) by titration with sodium hydroxide to a first end-point in the cold with phenolphthalein as indicator and then completing the titration at the b. p. These results were irrespective of the ratio $Cr_2(SO_4)_3 : H_2SO_4$ and of the total weight of chromium present. Chromium was determined by oxidation to the dichromate stage with ammonium persulphate (Vogel, " Quantitative Inorganic Analysis," Longmans Green & Co., 1948, p. 370). Anhydrous chromic sulphate could not be dissolved in water except in presence of chromous ions (cf. Sidgwick, " Chemical Elements and Their Compounds," Oxford, 1950, Vol. 2, p. 1013), and was analysed only for chromium by ignition to Cr_2O_3. Since the anhydrous phase was formed in boiling concentrated sulphuric acid, its water content was assumed to be less than 1·0% [cf. anhydrous $Al_2(SO_4)_3$].

Results. Analyses for all liquid and solid phases are given in the Table in compositions by weight. At 25° up to an acid concentration of about 10%, $Cr_2(SO_4)_3,16H_2O$ (A in the Table) is the stable solid phase and has an *X*-ray powder photograph identical with that of $Al_2(SO_4)_3,16H_2O$. The analytical values actually correspond more nearly to a 15-hydrate, but in view of the *X*-ray data, solid A must be the 16-hydrate. Between 10 and 30% of acid, a second form of the 16-hydrate (B in the Table) is obtained, and although the analytical values for A and B differ slightly, close similarity of *X*-ray powder photographs and identity of crystal habit (small violet elongated hexagonal plates) make it practically certain that the two have the same stoicheiometric composition and very similar geometrical configurations. In the range 30—45% of acid, the solid phase is the 14-hydrate (C in the Table). This was obtained only from solutions which initially were highly supersaturated, and occurs as minute, pale blue needles with a characteristic *X*-ray powder photograph. A tracer experiment with radiocæsium (cf. Taylor and Scott, *Nature*, 1951, **168**, 520) showed that phase C could not contain more that about 3% of sulphuric acid, and was therefore most unlikely to be an acid sulphate. Although no further solid phases could be obtained at higher acid concentrations even after 6 months' stirring, heating an approximately 5% chromic sulphate solution.in concentrated acid to the b. p. readily gave the anhydrous sulphate as a salmon-pink microcrystalline solid, whose *X*-ray powder photograph showed exactly the same pattern of spacings as that of anhydrous aluminium sulphate, the absolute values of the spacings being a few units % greater. The solid probably contains considerably more intercrystallite sulphuric acid than the corresponding aluminium compound. Also, a series of solid solutions of composition $(Al,Cr)_2(SO_4)_3,H_2SO_4,2H_2O$ was obtained by heating mixtures of aluminium and chromic sulphates in 80% sulphuric acid till fuming commenced. Each member of the series gave an *X*-ray powder photograph identical with that of the parent aluminium compound, but the crystal habit was quite different : small pale green needles (colour deepening with chromium content) instead of colourless regular hexagonal plates. With a molecular ratio $Cr_2(SO_4)_3 : Al_2(SO_4)_3 = 9$ in the liquid phase, the precipitated solid solution contained not more than 3 atoms of chromium to every 7 of aluminium, and it therefore appears unlikely that a pure chromium 1,1,2 compound could be prepared. Attempts to prepare acid chromic sulphates by adding " AnalaR " acetone to solutions containing about 10% of $Cr_2(SO_4)_3$ and 75—90% of H_2SO_4, and which had been stirred previously at 25° for several months, gave green, exceedingly deliquescent precipitates. These contained only 2—3% of free acid, and by *X*-ray powder photographs were shown to be amorphous. Apart from the 1,1,2 solid solutions, these were the only green solid phases encountered in this work; on the other hand, all saturated liquid phases were deep green.

The system $Cr_2(SO_4)_3$–H_2SO_4–H_2O at 245°.

Solution		Dry solid phase			Solution		Dry solid phase		
$Cr_2(SO_4)_3$, %	H_2SO_4, %	$Cr_2(SO_4)_3$, %	H_2SO_4, %	Solid phase	$Cr_2(SO_4)_3$, %	H_2SO_4, %	$Cr_2(SO_4)_3$, %	H_2SO_4, %	Solid phase
39·05	0·0	58·77	0·0	A	13·52	31·08	38·45 *	13·39 *	B
—	—	59·45	0·0	A	8·48	38·26	27·41 *	24·05 *	C
30·80	7·06	58·80	0·83	A	7·31	43·21	60·71	0·78	C
26·51	11·68	59·83	0·0	B	—	—	60·31	0·49	C
23·15	15·90	59·40	0·0	B	—	—	60·62	1·08	C
19·70	20·73	—	—	B	—	—	81·9 †	~18	Anhyd.
17·10	24·27	60·4	0·17	B	—	—	82·6 †	~17	Anhyd.

* Moist solid phase. † Temperature ~300°.

Solid phases : A and B = two forms of $Cr_2(SO_4)_3,16H_2O$ [Calc. : $Cr_2(SO_4)_3 = 57·6\%$].
C = $Cr_2(SO_4)_3,14H_2O$ [Calc. : $Cr_2(SO_4)_3 = 60·9\%$].

UNIVERSITY OF EDINBURGH.

[*Received, April 7th*, 1953.]

511. *The Methoxyl Content of Gum Tragacanth.*

By KEITH SELBY.

GUM TRAGACANTH, an exudation of shrubs of the genus *Astralagus*, has been claimed by James and Smith (*J.*, 1945, 739) to contain "methoxyl groups (OMe, 3·8%) of an etheric nature since the methoxyl content was unchanged by treatment of the gum with sodium hydroxide solution." Recent work in these laboratories has shown, however, that a portion of the uronic acids is esterified in the natural gum and that virtually the whole of the methoxyl content occurs in the form of methyl ester.

The evidence for this conclusion is based on changes in carboxyl and methoxyl contents of alkaline solutions of the gum on storage in the cold. In a typical experiment a sample of "medium flake" gum tragacanth (60 g.) was fractionated by dissolution in a dilute buffer solution [10^{-4}M-sodium acetate and $0·4 \times 10^{-4}$M-acetic acid] (10 l.). After several days in the refrigerator the swollen but undissolved material, bassorin, was removed by centrifugation and the soluble fraction, tragacanthin, was isolated (30 g.). This material (OMe, 3·38%; 0·5 g.) was allowed to react in solution (50 ml.) with potassium hydroxide (2·41 milliequiv.) at room temperature for periods of ½ to 72 hr. The carboxyl content of each sample was then determined by titration to pH 8. The solutions were immediately readjusted to the pH value of the natural gum and, after evaporation *in vacuo* with successive small quantities of water to remove any volatile alcohols, the methoxyl contents were determined by a semimicro-modification of the Zeisel method (Samsel and McHard, *Ind. Eng. Chem. Anal.*, 1942, **14**, 750) (see Table). Similar experiments with bassorin (OMe, 1·03%) and with the whole gum, as well as with samples of pharmaceutical quality (OMe, 2·00%), gave similar results.

Change (*milliequiv./g. of gum*) *in carboxyl and methoxyl contents of tragacanthin during saponification.*

Time (hr.)	CO_2H	OMe	Gain in CO_2H	Loss of OMe	Time (hr.)	CO_2H	OMe	Gain in CO_2H	Loss of OMe
0	0·26	1·08	—	—	2	1·16	0·22	0·90	0·86
½	0·78	0·44	0·52	0·64	72	1·37	0·04	1·11	1·04

It was established that no part of these changes was due to atmospheric oxidation. The viscosities of the solutions were unchanged during the saponification, showing that polymeric ester linkages were not involved. The close relation between gain in carboxyl content and loss of methoxyl content suggested that the change taking place was hydrolysis of methyl ester groups.

For confirmation of the production of methanol during saponification of tragacanthin, volatile alcohols produced were concentrated by fractional distillation. Oxidation with acidic potassium permanganate (Hoffpauir and Reeves, *Analyt. Chem.*, 1949, **21**, 815) yielded formaldehyde, characterised as its dimedone derivative, m. p. and mixed m. p. 190°.

THE BRITISH COTTON INDUSTRY, RESEARCH ASSOCIATION,
DIDSBURY, MANCHESTER, 20.

[*Received, April 7th*, 1953.]

---

512. 1 : 2-O-iso*Propylidene*-β-D-*altrofuranose.*

By F. H. NEWTH.

THE partial hydrolysis of 1 : 2-5 : 6-di-*O*-*iso*propylidene-α-D-glucofuranose under mildly acidic conditions to give 1 : 2-*O*-*iso*propylidene-α-D-glucofuranose is well known. The analogous reaction in the D-altrose series is now described. 1 : 2-5 : 6-Di-*O*-*iso*propylidene-β-D-altrofuranose (Steiger and Reichstein, *Helv. Chim. Acta*, 1936, **19**, 1011; Newth and Wiggins, *J.*, 1950, 1734), when treated with 80% acetic acid, lost one *iso*propylidene residue, and 1 : 2-*O*-*iso*propylidene-β-D-altrofuranose was formed in excellent yield.

Steiger and Reichstein assigned the *iso*propylidene residues to positions 1 : 2 and 5 : 6 in the D-altrofuranose molecule on the basis of steric considerations and the fact that the compound was not oxidised by permanganate. It is now possible to provide a more definite proof of its constitution. 1 : 2-5 : 6-Di-*O*-*iso*propylidene-β-D-altrofuranose formed a crystalline 3-*O*-toluene-*p*-sulphonate which failed to react with sodium iodide in acetone at 110°. This clear indication of the absence of a primary tosyloxy group is consistent with the resistance of the di-*O*-*iso*propylidene compound to oxidation. Furthermore, 3-*O*-methyl-1 : 2-5 : 6-di-*O*-*iso*propylidene-β-D-altrofuranose could also be selectively hydrolysed to 3-*O*-methyl-1 : 2-*O*-*iso*propylidene-β-D-altrofuranose; this reacted with one mol. of lead tetra-acetate, and one mol. of formaldehyde was liberated. The oxidisable glycol system must, therefore, be at $C_{(5)}$–$C_{(6)}$, the situation of the more labile *iso*propylidene residue. The other residue is certainly joined to $C_{(1)}$ since all the above compounds are non-reducing and there is little reason to suppose that it is a 1 : 3- rather than a 1 : 2-*O*-*iso*propylidene group.

Experimental.—1 : 2-O-iso*Propylidene*-β-D-*altrofuranose.* A solution of 1 : 2-5 : 6-di-*O*-*iso*-propylidene-β-D-altrofuranose (0·90 g.) in 80% acetic acid (20 ml.) was kept for 24 hr. and then evaporated to dryness at 65°. The residue was recrystallised from ethyl acetate, and 1 : 2-O-iso*propylidene*-β-D-*altrofuranose* was obtained as small cubes (0·65 g.), m. p. 125—126°, $[\alpha]^{17}_{D}$ +25·8° (*c*, 1·01 in MeOH) (Found : C, 48·8; H, 7·1. $C_9H_{16}O_6$ requires C, 49·1; H, 7·3%).

1 : 2-5 : 6-*Di*-O-iso*propylidene*-3-O-*tosyl*-β-D-*altrofuranose.* The di-*O*-*iso*propylidene compound (0·10 g.) was treated with toluene-*p*-sulphonyl chloride in pyridine solution. The 3-O-*tosyl* derivative had m. p. 100—101° (from alcohol), $[\alpha]^{20}_{D}$ +30·7° (*c*, 0·85 in $CHCl_3$) (Found : C, 54·9; H, 6·4. $C_{19}H_{26}O_8S$ requires C, 55·0; H, 6·3%). The compound was recovered quantitatively after 16 hr.' heating with sodium iodide in acetone solution at 110°. In one instance this derivative (4 g.) separated from the mixture of di-*O*-*iso*propylidene-*O*-tosyl-D-altrose compounds [syrup *B*] obtained from a D-altrose–1 : 6-anhydro-β-D-altropyranose mixture (25 g.) (Newth and Wiggins, *loc. cit.*).

Reduction of 1 : 2-5 : 6-*di*-O-iso*propylidene*-3-O-*tosyl*-β-D-*altrofuranose with sodium amalgam.* The compound (3·0 g.) was dissolved in 90% methanol (100 ml.), and sodium amalgam (3%, 60 g.) added. After being stirred overnight, the solution was decanted from the mercury, which was washed with methanol, and the combined solution and washings neutralised with carbon dioxide. The residue which was obtained when the solution was evaporated was extracted with chloroform. Evaporation of this extract provided 1 : 2-5 : 6-di-*O*-*iso*propylidene-β-D-altrofuranose (1·6 g.), m. p. 87—88° after 3 recrystallisations from ether–light petroleum.

3-O-*Methyl*-1 : 2-5 : 6-*di*-O-iso*propylidene*-β-D-*altrofuranose.* 1 : 2-5 : 6-Di-*O*-*iso*propylidene-β-D-altrofuranose (0·65 g.) was thrice treated with methyl iodide and silver oxide at 45°. The 3-O-*methyl* derivative (0·60 g.) distilled at 102° (bath)/0·05 mm. and had n^{23}_{D} 1·4499, $[\alpha]^{23}_{D}$ +4·0° (*c*, 1·24 in $CHCl_3$) (Found : C, 56·6; H, 7·8; OMe, 10·8. $C_{13}H_{22}O_6$ requires C, 56·9; H, 8·1; OMe, 11·3%).

3-O-*Methyl*-1 : 2-O-iso*propylidene*-β-D-*altrofuranose.* A solution of the above 3-*O*-methyl derivative (0·31 g.) in 80% acetic acid (10 ml.) was kept for 24 hr. and then evaporated at 65°. The syrupy residue distilled at 145° (bath)/0·04 mm.; the 3-O-*methyl*-1 : 2-O-iso*propylidene*-β-D-*altrofuranose* (0·22 g.) had n^{17}_{D} 1·4734, $[\alpha]^{18}_{D}$ +10·2° (*c*, 0·39 in MeOH) (Found : C, 51·1; H, 7·5. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7%). The compound consumed 0·955 mol. of lead tetra-acetate (5·3 hr.; 1·105 mol. after 20 hr.) under standard conditions. Formaldehyde (0·95 mol.), estimated as the dimedone derivative, m. p. 188—189°, was liberated during the reaction.

THE UNIVERSITY, BIRMINGHAM.
(Present Address : UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.)

[*Received, April* 24*th*, 1953.]