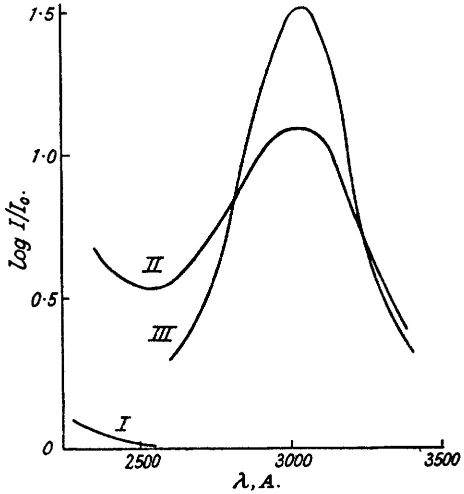
242. *The Reaction of Methyl Tetramethyl Glucosaccharate with Sodium.*

By L. F. WIGGINS.

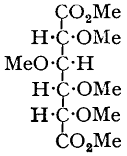
When methyl tetramethyl glucosaccharate is treated with sodium in toluene in the presence of a trace of methyl alcohol an unexpected reaction occurs. The product isolated is methyl 2 : 5-dimethoxymuconate, probably the *cis–trans* isomer. The relation of this phenomenon to that occurring when mannosaccharodilactone is treated with diazomethane (Schmidt and Kraft, *Ber.*, 1941, **74**, 33) is discussed.

TREATMENT of methyl 2 : 3 : 4 : 5-tetramethyl D-glucosaccharate (I) with sodium in boiling toluene containing a trace of methyl alcohol afforded an unsaturated crystalline compound, m. p. 118°. Analytical results showed that it had been formed from (I) by elimination of two molecules of methanol and that it had the formula $C_{10}H_{14}O_6$. Four methyl groups were present in the compound, and, of these, two were present as carbomethoxy-residues. The unsaturation of the compound was such as to give rise to a system which showed strong selective absorption of ultra-violet light. The same characteristic absorption band makes its appearance when methyl tetramethyl glucosaccharate is boiled for a few minutes in ethyl-alcoholic solution containing a drop of 5N-sodium hydroxide (see Fig.). The compound was evidently identical with methyl dimethoxymuconate (II) previously obtained by Haworth, Hirst, and Jones (*J.*, 1938, 710) and by Schmidt and Kraft (*Ber.*, 1941, **74**, 33). Confirmation of this structure (II) assigned to the unsaturated compound was forthcoming from the observation that it underwent

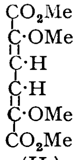


I. *Methyl* 2 : 3 : 4 : 5-*tetramethyl glucosaccharate* (*c*, 126·4 *mg. per* 100 *ml. in* EtOH).
II. *Methyl* 2 : 3 : 4 : 5-*tetramethyl glucosaccharate after being boiled for* 5 *minutes with* 1 *drop of* 5N-NaOH, *cooled, and diluted to* ca. 12·6 *mg. per* 100 *ml. in* EtOH. $\lambda_{max.}$ 3030 A., ε ca. 2500.
III. *Methyl* 2 : 5-*dimethoxymuconate* (*c*, 1·25 *mg. per* 100 *ml. in* EtOH). $\lambda_{max.}$ 3030 A., ε ca. 27,600. $\lambda_{max.}$ 3038 A., ε ca. 27,600.

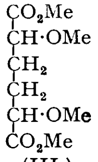
smooth catalytic hydrogenation with the consumption of four atomic proportions of hydrogen and formation of methyl *meso*-2 : 5-dimethoxyadipate (III) (Schmidt and Kraft, *loc. cit.*).



(I.)

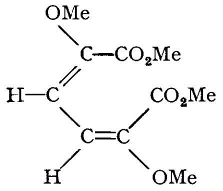


(II.)

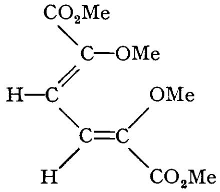


(III.)

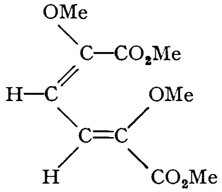
Methyl 2 : 5-dimethoxymuconate may exist in three forms, the *cis-cis* (IV), the *trans-trans* (V), and the *cis-trans* (VI), and the question arises as to which of these three is the product of m. p. 118° obtained by the action of sodium on methyl 2 : 3 : 4 : 5-tetramethyl D-glucosaccharate. When the elements of methyl alcohol are removed from C_2 and C_3 and C_4 and C_5 of the model of this compound, methyl *cis-trans*-2 : 5-dimethoxymuconate results. It would appear, therefore, that the methyl 2 : 5-dimethoxymuconate, m. p. 118°, is the *cis-trans*-isomer.



(IV.)



(V.)



(VI.)

On the other hand, when the elements of methyl alcohol are removed from C_2 and C_3, and C_4 and C_5 of the model of methyl 2 : 3 : 4 : 5-tetramethyl D-mannosaccharate to form methyl 2 : 5-dimethoxymuconate, the *trans-trans*-form is obtained. It is noteworthy that when Schmidt and Kraft (*Ber.*, 1941, **74**, 33) and Haworth, Heslop, Salt, and Smith (*J.*, 1944, 217) subjected mannosaccharodilactone to methylation with methyl iodide and silver oxide or to the action of diazomethane, they obtained, among other products, methyl 2 : 5-dimethoxymuconate, m. p. 140°, and in no case was the isomer, m. p. 118°, isolated. Thus, it is suggested that the substance, m. p. 140°, obtained by the two sets of workers mentioned previously is the *trans-trans*-isomer. This argument becomes invalid, however, if at any time a double bond is transitorily formed between C_1 and C_2 or between C_5 and C_6. The possible relationship between the different forms of dimethoxymuconic acid and the stereochemistry of their saccharic acid precursors are merely pointed out at this stage. There is no intention to state dogmatically the structures of the particular dimethoxymuconic acids discussed above. In view of these conclusions it is intended to examine the products of similar reactions with saccharic acids of different configurations.

EXPERIMENTAL.

Treatment of Methyl 2 : 3 : 4 : 5-*Tetramethyl* D-*Glucosaccharate with Sodium.*—Methyl tetramethyl D-glucosaccharate (2 g.) was dissolved in dry toluene (15 c.c.), and powdered sodium (0·5 g.) added. A few drops of dry methyl alcohol were added, and the mixture heated to boiling and continuously shaken for 1 hour. There was a brisk evolution of gas and separation of some tarry matter. The clear upper layer was decanted and the residue extracted several times with fresh toluene. The extracts were combined and evaporated to small bulk; the fine needles of methyl 2 : 5-dimethoxymuconate (0·3 g.) which separated, when recrystallised from toluene, had m. p. 117—118° and were optically inactive. The substance decolourised alkaline permanganate and bromine in carbon tetrachloride (Found : C, 52·5; H, 5·9; OMe, 53·9; equiv., 119. Calc. for $C_{10}H_{14}O_6$: C, 52·2; H, 6·1; OMe, 53·9%; equiv., 115). The yield was variable, the best being 0·4 g. from 1·1 g. of the methylated glucosaccharic acid ester.

Hydrogenation of Methyl 2 : 5-*Dimethoxymuconate.*—The crystals (0·4 g.) were dissolved in dry methyl alcohol, palladised charcoal containing 0·1 g. of palladium was added, and the mixture was shaken with hydrogen at slightly over atmospheric pressure. A rapid uptake of hydrogen occurred, and reaction was complete in 0·5 hour. The catalyst was filtered off and the solution evaporated. The oily residue distilled at 105°/0·03 mm. Yield 0·35 g. This methyl *meso*-2 : 5-dimethoxyadipate partly crystallised, and the crystals were separated on porous tile. After being recrystallised from ether–petrol, they had m. p. 52—53° (0·11 g.) (Found : C, 51·5; H, 7·8. Calc. for $C_{10}H_{18}O_6$: C, 51·3; H, 7·7%). Schmidt and Kraft (*loc. cit.*) record m. p. 53° for this substance. The porous tile employed for the separation of the crystalline material was extracted with boiling chloroform, the extract evaporated, and the residue distilled. It distilled at 100° (bath temp.)/0·03 mm. (0·2 g.) and showed $n_D^{20°}$ 1·4379. It was probably DL-methyl 2 : 5-dimethoxyadipate (Found : OMe, 52·0. Calc. for $C_{10}H_{18}O_6$: OMe, 53·0%).

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