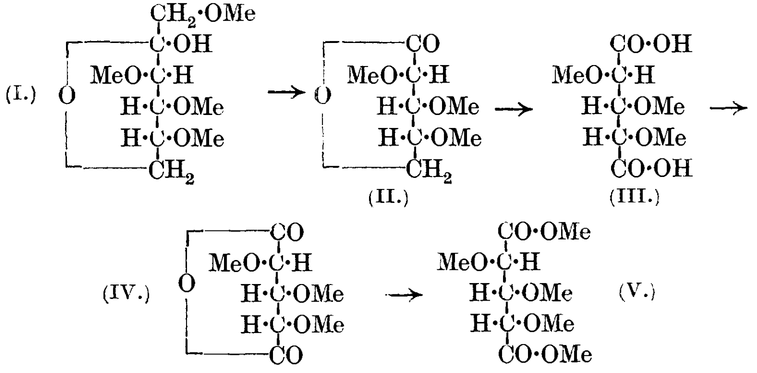
CCXXX.—*The Constitution of Sucrose. Part II. Evidence contributed by the Oxidation of* d-*Arabinose.*

By George McOwan.

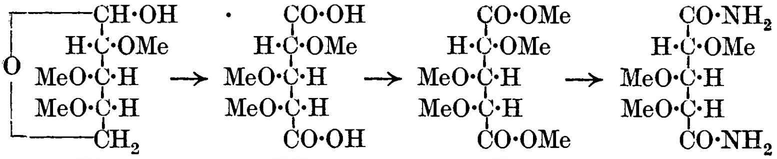
The conclusions drawn by Haworth and Linnell from the experimental results on the structure of γ-fructose applied by them to the constitution of sucrose (J., 1923, **123**, 294) involve an inconsistency which renders their arguments invalid.

By oxidising tetramethyl γ-fructose, Haworth and Linnell claim to have obtained a *dextrorotatory* dimethyl trimethoxyglutarate giving $[\alpha]_D + 48{\cdot}7°$ in water. As this product should retain the configuration of *d*-fructose, the fact that Haworth and Linnell reported a dextrorotation was opposed to what might reasonably have been expected, and that such objection is valid was subsequently revealed when Hirst and Robertson (J., 1925, **127**, 358) obtained from *l*-arabinose a dimethyl trimethoxy-*l*-glutarate which was dextrorotatory ($[\alpha]_D = + 45°$ in water). These contradictory results have remained unexplained and it is evident that a decision has to be made between the researches in question. The present communication confirms the work of Hirst and Robertson and, incidentally, provides additional evidence that the work of Haworth and Linnell on sucrose cannot be supported.

In order to place the position in proper perspective, it is necessary to review the series of reactions in which dimethyl trimethoxyglutarate was obtained in the constitutional studies referred to above. Haworth and Linnell oxidised tetramethyl γ-fructose (I) with nitric acid to trimethoxyvalerolactone (II), which was subsequently converted by alkaline permanganate into trimethoxyglutaric acid (III), identified as the anhydride (IV) and as the dimethyl ester (V).



On the other hand, dimethyl trimethoxyglutarate was encountered by Hirst and Robertson in studying the constitution of trimethyl *l*-arabinose (VI), which on oxidation yielded trimethoxyglutaric acid (VII); this was identified as the dimethyl ester (VIII) and as the crystalline diamide (IX):



(VI.) (VII.) (VIII.) (IX.)

The arabinose employed by the latter workers was the naturally occurring *l*-arabinose, which is dextrorotatory, $[\alpha]_D = + 104{\cdot}4°$ (Scheibler, *Ber.*, 1884, **17**, 1731; Lippman, *ibid.*, p. 2239), and the trimethyl arabinose and dimethyl trimethoxyglutarate derived from it also have marked dextrorotatory powers, $[\alpha]_D = + 127{\cdot}22°$ (Purdie and Rose, J., 1906, **89**, 1204), and $[\alpha]_D = + 47{\cdot}3°$ (Hirst and Robertson, *loc. cit.*), respectively. Oxidation of unsubstituted *l*-arabinose (Kiliani, *Ber.*, 1888, **21**, 3007) yields a trihydroxyglutaric acid which is lævorotatory, $[\alpha]_D = - 22{\cdot}7°$ (Fischer, *Ber.*, 1891, **24**, 1844), but when this is converted into dimethyl trimethoxyglutarate the sign of the rotation is changed and an ester identical in every respect with (VIII) is obtained (Hirst and Robertson, *loc. cit.*).

The pentose which is structurally related to *d*-fructose is, however, the *d*-arabinose which can be prepared by the degradation of *d*-glucose. In solution it yields an equilibrium mixture of the α- and β-forms of the sugar showing a specific rotation equal to that displayed by the natural sugar, but of opposite sign (Wohl, *Ber.*, 1893, **26**, 730; Ruff, *Ber.*, 1899, **32**, 553; Weerman, *Rec. trav. chim.*, 1917, **36**, 16; 1918, **37**, 16). On oxidation by Kiliani's method, *d*-arabinose yields a trihydroxyglutaric acid ($[\alpha]_D = + 22{\cdot}28°$; Ruff, *loc. cit.*) which is the optical enantiomorph of that obtained from *l*-arabinose. In a parallel manner the oxidation of trimethyl *d*-arabinose should give rise to a trimethoxyglutaric acid the dimethyl ester of which should be enantiomorphous with (VIII). The present communication deals with this series of reactions.

It has been ascertained that the methylation of *d*-arabinose proceeds in a manner exactly parallel to that of *l*-arabinose as described by Purdie and Rose (*loc. cit.*). The optical activity of the methylated sugar is also of the same order but, as was to be expected, is opposite in sign. Oxidation of trimethyl *d*-arabinose yields a trimethoxyglutaric acid, identified as the dimethyl ester and the crystalline diamide, the compounds being optical enantiomorphs of those (VIII and IX) described by Hirst and Robertson. The ester obtained by Haworth and Linnell should be the same as that obtained in this investigation and should be the enantiomorph of that described by Hirst and Robertson. Such is not the case, as will be evident from inspection of the results quoted below :

	Rotations of *d*- and *l*-dimethyl trimethoxyglutarates.		Rotations of Haworth and Linnell's (?) dimethyl trimethoxyglutarate.
	A.*	B.†	C.‡
Source.	*l*-Arabinose.	*d*-Arabinose.	Sucrose.
$[\alpha]_D$ (water)	+45° (*c*, 1·46)	−42·5° (*c*, 1·26)	+48·7° (*c*, 0·72)
$[\alpha]_D$ (MeOH)	+47·3° (*c*, 1·84)	−47·5° (*c*, 1·9)	—

* Hirst and Robertson (*loc. cit.*). † Present communication.
‡ Haworth and Linnell (*loc. cit.*).

It is obvious that product C should show the same specific rotation as product B and should equally be the enantiomorph of A. The result quoted by Haworth and Linnell cannot be reconciled with this conclusion and the discrepancy disposes of the arguments upon which Haworth developed his formula for sucrose.

EXPERIMENTAL.

Preparation of d-*Arabinose.*—*d*-Arabinose was prepared according to the methods described by Weerman (*loc. cit.*), by the action of a solution of sodium hypochlorite on *d*-gluconamide, which was obtained from *d*-gluconolactone prepared by the action of freshly-precipitated yellow mercuric oxide on *d*-glucose (Heffter, *Ber.*, 1889, **22**, 1049). *d*-Gluconamide showed, in agreement with the figures quoted by Weerman, $[\alpha]_D$ in water = + 33·4° for c = 1·23; m. p. 142—143°. The experimental procedure followed closely that of Weerman, and the hypochlorite solution was prepared as described by him. *d*-Arabinose was isolated through the diphenylhydrazone (Neuberg, *Z. physiol. Chem.*, 1902, **35**, 34), which was decomposed in portions of 5 g. by boiling with freshly-distilled formaldehyde solution (Neuberg, *Ber.*, 1900, **33**, 2248). *d*-Arabinose was obtained as a colourless, crystalline product as described by Weerman. It showed $[\alpha]_D$ in water = − 117·9° falling to − 102·1° in 24 hours; m. p. 156—157°, m. p. of the diphenylhydrazone, 202—203° (compare Weerman, *loc. cit.*; $[\alpha]_D$ in water = − 105·7°; m. p. 156—157°; m. p. of the diphenylhydrazone 202—203°). The yield of *d*-arabinose diphenylhydrazone was 40% of the theoretical; Weerman quotes 49·4%.

Methylation of d-*Arabinose.*—A solution of 12·5 g. of *d*-arabinose in 62·5 g. of methyl alcohol containing 0·25% of hydrogen chloride was heated in a sealed tube as described by Fischer (*Ber.*, 1895, **28**, 1156). On concentrating the alcohol to a third of its volume, α-methylarabinoside was obtained as a colourless, crystalline product, which, on recrystallisation from methyl alcohol, showed $[\alpha]_D^{16^\circ} = -241{\cdot}07^\circ$ in water for $c = 1{\cdot}12$, m. p. 168° (compare Purdie and Rose; $[\alpha]_D = +245{\cdot}7^\circ$, m. p. 165—166°). Yield 5 g.

4·5 G. of α-methylarabinoside were methylated twice with methyl sulphate (25 c.c.) and sodium hydroxide (20 g. dissolved in 43 c.c. of water). The product was isolated by the usual methods as a colourless, mobile syrup, 3·5 g. being obtained on distillation (b. p. 135°/25 mm.; $n_D^{16^\circ}$ 1·4590). This did not crystallise on standing, but after a further methylation with silver oxide (18 g.) and methyl iodide (30 g.) and isolation of the product (b. p. 126°/30 mm.) as usual, crystallisation set in immediately. 3 G. of colourless crystals of trimethyl α-methylarabinoside were obtained which after draining on tile had the following properties: $[\alpha]_D^{16^\circ}$ in methyl alcohol $= -217{\cdot}53^\circ$, for $c = 1{\cdot}164$; $n_D^{25^\circ} = 1{\cdot}4452$ for superfused material; m. p. 43—45° (compare Purdie and Rose; $[\alpha]_D = +223{\cdot}08^\circ$; m. p. 43—45°) (Found: C, 52·2; H, 8·7; OMe, 61·4. Calc.: C, 52·4; H, 8·7; OMe, 60·2%).

Oxidation and Simultaneous Hydrolysis of Trimethyl α-Methylarabinoside.—1·7 G. of trimethyl α-methylarabinoside were oxidised with 40 c.c. of nitric acid (*d* 1·2) and the product was isolated as the methyl ester by the method described by Hirst and Purves (*loc. cit.*). 1·7 G. of a colourless, mobile syrup were obtained with the following properties: b. p. 143°/15 mm., $n_D^{16^\circ}$ 1·4375, $[\alpha]_D^{16^\circ}$ in methyl alcohol $= -47{\cdot}5^\circ$ for $c = 1{\cdot}98$, $[\alpha]_D^{16^\circ}$ in water $= -42{\cdot}5^\circ$ for $c = 1{\cdot}259$ (Found: C, 48·1; H, 7·1; OMe, 61·5. Calc. for dimethyl trimethoxyglutarate, $C_{10}H_{18}O_7$: C, 48·0; H, 7·2; OMe, 62·0%).

Trimethoxyglutaramide.—The identity and purity of the ester were further confirmed by converting it into the corresponding diamide by standard methods. This showed m. p. 232—233°, $[\alpha]_D^{16^\circ}$ in water $= -49{\cdot}54^\circ$ for $c = 0{\cdot}545$ (Found: OMe, 41·9. Calc.: OMe, 42·3%).

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