

mixtures. The portion insoluble in light petroleum ( $[\alpha]_D^{20} = -20^\circ$  in chloroform), on complete methylation can be divided into two fractions, a crystalline body ( $X$ ), and an oil, whilst the soluble portion ( $[\alpha]_D^{20} = +40^\circ$ ) can be distilled in a high vacuum to yield two fractions: ( $A$ ) of b.p.  $160^\circ/0.09$  mm. (bath temp.),  $[\alpha]_D^{18} = +59^\circ$  in chloroform; and ( $B$ ) of b.p.  $178^\circ$  (bath temp.)/ $0.09$  mm.  $[\alpha]_D^{18} = +25^\circ$ . Complete methylation of these subfractions gave rise to a mixture of ( $X$ ) and an oil from ( $A$ ) and a large yield of the crystalline material ( $X$ ) from ( $B$ ). In the same way the syrup obtained from the mother liquors after recrystallization of the 2:4:6-trimethyl methylgalactoside was partially transformed by methylation into ( $X$ ).

On account of the difficulties in manipulation, it is not easy to estimate precisely the yield of this substance ( $X$ ), but it appears to be about 16 per cent of the weight of methylated agar employed. It is non-reducing and has b.p.  $85-90^\circ/0.05$  mm., m.p.  $81^\circ$  and  $[\alpha]_D^{20} = +75^\circ$  in water and  $+85^\circ$  in chloroform. Analysis showed it to have the composition  $C_6H_{10}O_2(OCH_3)_2$  and it is therefore a dimethyl anhydro methylhexoside. It gave a strong Seliwanoff test and simulated a furanoside on account of the ease of removal of the glycosidic residue by dilute mineral acid; it was found that hydrolysis to the free anhydro-sugar ( $[\alpha]_D^{18} = -23^\circ$ ) took place by contact for 24 hours with *N*-sulphuric acid. This resembles the behaviour of the 3:6-anhydro-2:4-dimethyl methylglucoside of Peat and Wiggins<sup>3</sup>, so that although the positive Seliwanoff reaction seemed anomalous, the chance that it might be a 3:6-anhydro-galactose derivative was considered. By the direct methylation of 3:6-anhydro- $\alpha$ -methylgalactoside prepared by the method of Ohle and Thiel<sup>4</sup>, the corresponding 2:4-dimethyl derivative was prepared. This substance was obtained as an oil, b.p.  $90^\circ/0.05$  mm.,  $n_D^{18} = 1.4640$  and  $[\alpha]_D^{20} = +87^\circ$  in chloroform. It is important to note that both these 3:6-anhydro-galactosides give the Seliwanoff reaction.

Although hydrolysis of the 2:4-dimethyl 3:6-anhydro- $\alpha$ -methylgalactoside in cold *N*-sulphuric acid was complete in 24 hours, the equilibrium value reached was  $[\alpha]_D^{18} = +22^\circ$  instead of  $-23^\circ$ , and although the general properties of the two substances are so similar that it is probable that the natural product is a 3:6-anhydride, it is clearly not 3:6-anhydro-2:4-dimethyl  $\alpha$ -methyl-*d*-galactoside, and further synthetic experiments will be necessary to decide its constitution. The fact that the specific rotations of the free dimethyl anhydro-sugar from agar and of 2:4-dimethyl 3:6-anhydro-*d*-galactose are approximately equal and opposite in sign makes it possible that the sugar concerned is not *d*- but *l*-galactose; this sugar has already been found in agar by Pirie<sup>5</sup>.

These experiments fail to support the suggestion previously advanced<sup>2</sup> that a ketose is present in the hydrolysis products of methylated agar, although accompanying ( $X$ ) is an oil of high methoxyl content which may be a fully methylated ketose; but little reliance can be placed on colour reactions in this case since the syrup may still contain a quantity of ( $X$ ).

It is impossible at present to decide whether the anhydride ring is preformed in agar or whether it is the result of side reactions. However, the former view is considered to be the most likely because of the low methoxyl and acetyl contents of methylated and

acetylated agar, which can be explained by the presence of the anhydro-hexose residues in the chain form each carrying only one hydroxyl free for substitution. The anhydro-hexose is clearly not an 'end group', since if it were, simple hydrolysis would set free the dimethyl anhydro-methylhexoside, whereas actually further methylation is necessary after hydrolysis. It is hoped to report upon the precise nature of the supposed 3:6-anhydro-dimethyl hexose and of the other unidentified products in due course.

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<sup>1</sup> Percival, Munro and Somerville, *NATURE*, 139, 512 (1937).

<sup>2</sup> Percival and Somerville, *J. Chem. Soc.*, 1615 (1937).

<sup>3</sup> Peat and Wiggins, *J. Chem. Soc.*, 1088 (1938).

<sup>4</sup> Ohle and Thiel, *Ber.*, 66, 525 (1933).

<sup>5</sup> Pirie, *Biochem. J.*, 30, 369 (1936).

### Multipolar Cyclohexane Rings

ON bromination, the isomeric forms of 1-carboxy-4-methylcyclohexane-1-acetic acid (m.p.  $173^\circ$  and  $137^\circ$ )<sup>1</sup> furnished monobromo acids, which gave the corresponding hydroxy acids on being heated with aqueous sodium carbonate. Oxidation of the hydroxy acids with alkaline permanganate gave rise, however, to isomeric forms of 4-methylcyclohexane-1:1-dicarboxylic acid, which depressed each other's melting points. Similar observations were made in the 3-methylcyclohexane series.

A full report of these experiments will be published in due course.

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<sup>1</sup> Desai, Hunter, Ghulam Khan and Saharia, *J. Chem. Soc.*, 416 (1936).

### Combustion Pressures in Spark-Ignition Engines

IT has come to the notice of investigators interested in combustion and detonation in spark-ignition engines that the combustion pressures may attain values which, even when no heat losses are considered, appeared to surpass those found by calculation, making use of the normally accepted data for such processes. The inadequacy of pressure indicating apparatus, especially when measurements were made under conditions of incipient or even persistent detonation, has for long prevented adequate attention being paid to this phenomenon.

Repeated measurements on different engines with Farnboro, quartz and capacity type indicators have now shown that the pressure rise over the compression pressure may in several cases be up to 50 per cent higher than is accounted for by classical calculations. The extreme cases occur when there is a certain degree of detonation, the phenomenon being then sometimes, though not always, accompanied by superimposed pressure vibrations; when these vibrations occur, the value cited relates to the mean value of the pressure.

These pressures being sustained beyond the period of vibration either of the gas mass or of the indicator, they must be considered as static pressures, to be