required β-diacetylenic acid (IV) as glistening plates, melting point 42–43°. Unfortunately, the high temperature needed for decarboxylation caused considerable resinification, and the yield of acid (IV) was correspondingly low; investigations to obviate this difficulty are now in progress.

A preliminary catalytic partial hydrogenation of the acid (IV) furnished a yellow oil which was identified as linoleic acid (V) by formation of its solid tetrabromide, melting point 112–113°, and by complete hydrogenation to stearic acid.

This work is being expanded and will be fully reported elsewhere. We are indebted to Sir Ian Heilbron and Prof. E. R. H. Jones for their interest in this work, which was carried out during the tenure of an I.C.I. Fellowship (R. A. R.) and a senior award of the Department of Scientific and Industrial Research (F. S.). Thanks are due to the Chemical Society for a research grant.

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[1] *J. Amer. Chem. Soc.*, **70**, 1699, 3391 (1948).

[2] Ralston, A. W., "Fatty Acids and their Derivatives" (Chapman and Hall, London, 1948).

[3] Rosenberg, H. R., "Chemistry and Physiology of the Vitamins", 531 (Interscience Publishers, New York, 1942).

[4] Grignard, V., and Lapayre, L., *C.R. Acad. Sci., Paris*, **192**, 250 (1931). Tchao Yin Lai, *Bull. Soc. Chim.*, **53**, 1537 (1933).

Preparation of Ethynylcarbinols from the Bisulphite Compounds of Aldehydes and Ketones

Whereas a variety of methods for the preparation of ethynylcarbinols from both saturated and unsaturated carbonyl compounds have been described[1], we have traced only one reference[2] in the literature to the preparation of diethynyl glycols, from dicarbonyl compounds and acetylene. While this work was in progress, Milas *et al.*[2] reported the preparation of the diethynyl glycols from diacetyl and acetonylacetone.

While aliphatic dialdehydes in particular are not easily accessible materials of low stability, their bisulphite compounds can frequently be obtained in a pure crystalline condition, and we find their purity readily determined by weighing the washed and dried precipitate formed by treatment with an excess of a standard solution of 2 : 4-dinitrophenylhydrazine sulphate.

We have now found that reasonable yields of ethynylcarbinols can be obtained from the bisulphite compounds of aldehydes and ketones by reaction with sodium acetylide in liquid ammonia. By this means the following pure ethynylcarbinols have been prepared in the yields stated: dimethylethynylcarbinol in 45 per cent yield, *n*-butylethynylcarbinol (32 per cent), phenylethynylcarbinol (45 per cent) and styrylethynylcarbinol (12 per cent), from the crystalline sodium bisulphite compounds of acetone, *n*-butaldehyde, benzaldehyde and cinnamaldehyde respectively. Styrylethynylcarbinol has previously been obtained in only 2 per cent yield[3] by reaction of cinnamaldehyde with sodium acetylide in liquid ammonia, and the method thus represents an improvement in this case.

Full details will be reported elsewhere; the application of the method to dicarbonyl compounds is under investigation.

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[1] Johnson, "The Chemistry of the Acetylenic Compounds" (Edward Arnold, London, 1946).

[2] Milas, Brown and Phillips, *J. Amer. Chem. Soc.*, **70**, 2862 (1948).

[3] Jones and McCombie, *J. Chem. Soc.*, 733 (1942).

Effect of Light on the Reaction between Periodates and α-Glycols

Since the original discovery by Malaprade of the cleavage of α-glycols by periodic acid and its salts, the reaction has been widely and increasingly used in the solution of structural problems connected with the carbohydrates. The course of the main Malaprade reaction with α-glycols and various compounds of similar type is well known, and the consumption of periodate is usually stoichiometric; but the literature contains many references to examples of so-called 'over-oxidation', or 'over-utilization', of periodate.

The cause of this may well vary from case to case; for example, I have shown[1] that whereas β-methyl glucoside and β-methyl cellobioside are oxidized stoichiometrically at $pH < 5$, very substantial over-oxidation occurs when the solutions are made alkaline. A factor of more general importance, which does not seem to have been noted hitherto, is the effect of light upon the course of the reaction.

Jackson and Hudson[2] and Davidson[3] observed that the amount of periodic acid or sodium *meta*periodate consumed in the oxidation of cellulose did not cease at the 'theoretical' value of one mole per C_6 unit, and figures as high as 1·22 for cotton and 1·86 for filter paper were reported. Davidson noted, too, the formation of considerable quantities of formic acid, formaldehyde and carbon dioxide, and it was evident that side reactions were occurring with both oxidants.

However, when I repeated Davidson's oxidation of cotton with sodium *meta*periodate, I found that the reaction virtually ceased when one mole of oxidant had been consumed (about twenty days at 20°), and even at the end of forty-one days the consumption was only 1·06 moles. A possible explanation of this discrepancy seemed to be that various chance circumstances had resulted in the almost complete shielding of the reaction mixture from light.

It has now been observed that with 1·6 moles of sodium *meta*periodate per C_6 unit, the oxidation of cotton at room temperature, and in the complete absence of light, virtually ceased when one mole of periodate had been consumed (about seventeen days in a particular experiment). When the reaction mixture was contained in a clear glass bottle accessible to bright daylight, oxidation was much more rapid and continued until all the available periodate had been consumed (1 mole after six days and 1·6 after eighteen days). With a much larger excess of periodate (3·7 moles $NaIO_4$ per C_6 unit) the consumption reached one mole in four days and 3·7 in twenty-five days when bright daylight was accessible to the reaction mixture.

The disappearance of periodate is followed in all cases by the appearance of free iodine; carbon dioxide can be detected, and the insoluble oxidized cotton has an appreciable carboxyl content not to be accounted for on the basis of the accepted mechanism of oxidation.

Similar results have been obtained for the oxidation of β-methyl glucoside and β-methyl cellobioside with sodium *meta*periodate. With a large excess of oxidant, the reaction does not terminate when the consumption of periodate and production of formic acid have reached the limits set by the classical Malaprade reaction, unless the experiment is carried out in complete darkness. In bright daylight, oxidation proceeds more rapidly and goes very much further.

There are very great variations in the rates of oxidation of different α-glycols (carbohydrates, glycosides, etc.) by periodate. It is probable that the disturbance of the normal reaction caused by irradiation is most pronounced when the 'dark reaction' is relatively slow, as it is in the oxidation of cellulose.

It is worthy of note that solutions of sodium *meta*periodate are themselves unstable when kept in bright daylight (for example, the concentration of a $0 \cdot 03\,M$ solution fell by about 10 per cent during fifteen days), and the odour of ozone first observed by Rammelsberg[4] is very pronounced. Solutions kept in the dark are both odourless and stable; illuminated reaction mixtures of sodium *meta*periodate with cotton or the glycosides do not smell of ozone.

Such evidence as is yet available points to the occurrence of far-reaching degradation during the photochemical reaction. The investigation of the subject is being continued in these laboratories.

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[1] *J. Text. Inst.*, **38**, *T*389 (1947).
[2] *J. Amer. Chem. Soc.*, **59**, 2049 (1937).
[3] *J. Text. Inst.*, **32**, *T*109 (1941).
[4] *Pogg. Ann.*, **134**, 534 (1868).

Isolation of a Saponin from the Heart-wood of the Mora Tree and of a Related Species, Morabukea

IN the course of a chemical examination of the wood of the mora tree, *Mora excelsa* (Benth.), from British Guiana and from Trinidad, we observed that the heart-wood contains an unusually high proportion of material soluble in water or alcohol, of which up to about one-half was found to consist of a saponin.

The saponin is most readily isolated by exhaustive extraction of the wood with hot alcohol, evaporation of the alcoholic liquor nearly to dryness, and trituration of the dark-coloured syrup with an excess of hot acetone. The colouring matter and other impurities pass into solution in the acetone, leaving a light-coloured amorphous solid, which is separated and purified by further treatment with acetone. The saponin is finally obtained as a very pale buff- or pink-coloured powder, the aqueous solution of which exhibits intense foaming properties. The saponin content of the heart-wood of a number of samples of mora from British Guiana was found to lie between 2·8 and 9·6 per cent, based on the dry weight of the wood. A saponin has also been found in the heart-wood of mora from Trinidad, and of the related species morabukea (*Mora gonggrijpii* (Kleinh.) Sandwith); but these woods have not been examined quantitatively. Although saponins are known to occur in small quantities in the wood of the boles of a few tree species[1], the wood of mora may prove to be a relatively rich source.

On hydrolysis with 6 per cent alcoholic hydrochloric acid for 30 min. at the boiling point, mora saponin yielded 21·4 per cent of a crude crystalline aglycone. Fractional crystallization of this product from ethyl alcohol resulted in the isolation, first, of a crystalline sapogenin of melting point 269–270° and $[\alpha]_D + 29 \cdot 5°$ ($c = 0 \cdot 83$ in chloroform) in a yield of 9·4 per cent of the dry weight of the original saponin (found: C, 76·67; H, 10·63 per cent). This sapogenin readily forms a monoacetate of melting point 255–257° (found: C, 76·91; H, 10·14 per cent). At least one other crystalline sapogenin is known to be present in the hydrolysis product of the original saponin. These substances are being further examined by Dr. D. H. R. Barton, to whom we are indebted for the suggestion that the principal sapogenin of melting point 269–270° is a new triterpenoid hydroxy-carboxylic acid.

Hydrolysis of mora saponin with 5 per cent aqueous sulphuric acid at 95° for 4 hr. gave a mixture of sugars from which the aglycone was separated by filtration. After neutralization of the filtrate with barium carbonate and evaporation to dryness, the sugars were extracted with 90 per cent ethyl alcohol and isolated as a concentrated syrup. Examination of the syrup by partition chromatography on paper[2] revealed the presence of two sugars, which were probably glucose and xylose.

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[1] Wise, L. E., *et al.*, "Wood Chemistry", 436 (Reinhold, New York, 1944).
[2] Partridge, S. M., *Nature*, **158**, 270 (1946).

Preparation of Carbonate-free Sodium Hydroxide

WE have been studying the carbonate – hydroxide ion exchange on the strong base resin 'Amberlite IRA-400' (manufactured by Rohm and Haas Company and supplied by Messrs. Charles Lennig and Co., Ltd., 1–11 John Adam Street, London, W.C.2). It was expected that the bivalent ion would be preferentially held by the resin, and this is so. The following figures show the results of bringing the resin in the carbonate form into equilibrium with various sodium hydroxide solutions.