contains the same amount of total yellow pigments as a ripe banana, but in the case of the former the yellow color is masked by chlorophyll.

Acknowledgment

The writer wishes to express his appreciation to Dr. F. M. Schertz of the Bureau of Soils at Washington, D. C., for his kindness in supplying a sample of pure chlorophyll.

Conclusions

The pigments, chlorophyll (a + b), xanthophylls and carotin were determined in the peel of bananas. From the data obtained the following conclusions have been reached: the data indicate that the chlorophyll content of the peel ranges from 102.9 to 51.7 milligrams per kilogram of fresh peel in the unripe fruit at discharge from the boat and decreases as the fruit ripens. Chlorophylls decrease as a straight line function of time (Fig. 3). The total yellow pigments (xanthophyll plus carotin) remain approximately constant throughout the maturation of the fruit. The amount of xanthophylls is always greater than the amount of carotin, the range of the former being from about 5 to 7 milligrams per kilogram of fresh peel, while the range of the latter is from 1.5 to 3.5 milligrams per kilogram of fresh peel.

Boston, Massachusetts

[Contribution from the Polarimetry Section of the Bureau of Standards, United States Department of Commerce]

THE STRUCTURE OF ALPHA-METHYLXYLOSIDE[1]

By F. P. Phelps and C. B. Purves

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Crystalline trimethylxylose, derived from the corresponding β-methylglycoside, was the first member of the methylated monosaccharides to which an amylene oxide ring structure could be assigned with certainty,[2] and at the time the opinion was expressed that not only α- and β-methylxyloside, but possibly xylose itself, were similarly constituted. The intervening years, however, have brought to light several cases in which methylating agents, applied to a reducing sugar, have produced derivatives of more than one ring type and, in this connection, the behavior of galactose and arabinose may be cited.[3] Pryde, Hirst and Humphries have shown that in the case of these two sugars methylation with methyl sulfate and alkali undoubtedly gives at least two ring forms. In the case of xylose also this method gives an impure product, the rotation

[1] Publication approved by the Director of the Bureau of Standards.

[2] Hirst and Purves, *J. Chem. Soc.*, **123**, 1352 (1923).

[3] Pryde, Hirst and Humphries, *ibid.*, **127**, 348 (1925).

of the methylated products being too low in addition to the yield being small. Our own values using this method are in approximate agreement with those of Carruthers and Hirst,[4] using the same method, and are much lower than the values obtained when pure α- or β-methylxyloside was methylated with silver oxide and methyl iodide. Likewise, it is now well known that the condensation of a reducing sugar with acid methyl alcohol, if carried out at room temperature, yields a γ-methylglycoside, while at higher temperatures such as Fischer used a mixture containing largely the α- and β-forms is obtained. Our own work indicates that all three are formed at an intermediate temperature and that the equilibrium reached in acidified methyl alcohol is not an equilibrium between the α- and β-forms only but between the α-, β-, γ- and perhaps other forms as well, the predominating form being determined by the conditions, temperature playing a particularly important role. As only two of these three forms can have the same ring structure, the third must have a different ring and there is no known way to tell which, if either, of these rings exists in the parent sugar. It accordingly follows that any conclusions regarding the identity of ring structure in the sugar series, to be satisfactory, must be based upon nothing less than a direct experimental identification and correlation of the derivatives concerned. Such a correlation has now been made for α- and for β-methylxyloside.

The earlier methylations of this sugar were carried out by Carruthers and Hirst,[4] who used methyl sulfate and caustic soda to prepare the β-form and who used Fischer's method to condense xylose with methyl alcohol for the α-form. In the latter case after that portion of the β-methylxyloside which crystallized from the product had been removed, the residual crude sirup was treated with silver oxide and methyl iodide and gave a mobile liquid with the elementary composition of a fully methylated pentose. When heated in acid methyl alcohol it displayed a final specific rotation of 50.4°, a value in good agreement with that of 49.5° acquired by trimethyl-β-methylxyloside under similar circumstances. Such behavior has long been known to be characteristic of an α-β pair of methyl glycosides possessing the same ring structure,[5] and the reasonable inference was made that one more example of the same phenomenon had been encountered. While, therefore, it is true that trimethyl-α- and -β-methylxyloside have been correlated, the method used was an indirect one and a series of considerations led the present authors to doubt its reliability in this case. Thus the methylated glycosides examined by the former workers did not conform to the decisive test of similar ring structure devised by Purdie and Irvine[5] in that trimethyl-β-methylxyloside, when hydrolyzed with aqueous acid, yielded a

[4] Carruthers and Hirst, *J. Chem. Soc.*, **121**, 2299 (1922).

[5] Purdie and Irvine, *ibid.*, **104**, 9 (1904).

crystalline trimethylxylose, $[\alpha]_D$ 20° in water, while the impure α-isomer gave rise to a levorotatory sirup. Moreover, the correlation adopted by Carruthers and Hirst is not valid if two trimethylxyloses, differing in ring type, happen to possess similar equilibrium rotations in acid methyl alcohol, a possibility which cannot be counted remote when it is remembered that Haworth and Westgarth[6] have recently prepared a second trimethylxylose with a specific rotation of 31.2° in water, or within 12° of the former figure. Third, in the preparation of trimethyl-β-methylxyloside from xylose by the methyl sulfate and sodium hydroxide, there is some uncertainty because of the small yield obtained, together with the suspicion that this method does not always yield a single product. If the trimethyl-β-methylxyloside contained a large unknown percentage of a second compound of similar properties and therefore difficult to separate and, as in this case, on hydrolysis yielded less than 50% of the theoretical amount of trimethylxylose, it would be difficult to say which of the two components in the parent mixture produced the trimethylxylose. A fourth consideration lay in the fact that α-methylglucoside, galactoside and arabinoside are directly correlated, in each case, to methylated derivatives which very probably possess an amylene oxide ring.[7] It follows that a similar structure must be assigned to the glycosides themselves and, if this is so, a computation in molecular rotations by the method of Hudson[8] leads to the conclusion that the 1:5 oxygen linking is not present in α-methylxyloside. As this is at variance with the accepted structure for the β-isomer, Dr. C. S. Hudson requested us to repeat the work of Carruthers and Hirst and to obtain more decisive experimental evidence on the matter.

The carefully purified crystalline α-methylxyloside was methylated by the silver oxide reaction and every care was taken to render the methylation complete. Although the trimethyl-α-methylxyloside could not be made to crystallize and purification was carried out by the uncertain method of distillation, the specific rotations determined, 121.7° in chloroform, 112.7° in water and 122° in methyl alcohol, are regarded as approximately correct. When methylated in similar fashion β-methylxyloside gave an excellent yield of the crystalline, fully methylated derivative. Purification was rigorous and the final constants were: m. p. 51°; $[\alpha]_D^{20}$ −69.5° in chloroform and −81.7° in water. Aqueous acid, of a lower concentration and at a lower temperature than that previously employed, hydrolyzed both trimethylmethylxylosides, 80–85% of the theoretical yield of crystalline trimethylxylose being isolated in each case. The two

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[6] Haworth and Westgarth, *J. Chem. Soc.*, **129**, 880 (1926).

[7] Charlton, Haworth and Peat, *ibid.*, **129**, 89 (1926); Hirst, *ibid.*, **129**, 350 (1926); Hirst and Robertson, *ibid.*, **127**, 358 (1925); Haworth, Ruell and Westgarth, *ibid.*, **125**, 2468 (1924).

[8] Hudson, THIS JOURNAL, **48**, 1434 (1926).

specimens of the sugar were then compared with each other and found to be identical. Mutarotation in water was swift, the initial specific rotation being 65° and the equilibrium rotation 17.7° in place of the value of 20° hitherto accepted as standard. Trimethylxylose occasionally displayed mutarotation in chloroform solution, the initial value of $[\alpha]_D^{20}$ 58° diminishing to 24°; also, the initial rotation to this solvent was quite erratic, lying anywhere between 58 and 45° after recrystallization from ether solution. In these cases it is possible that the sugar crystallized as a mixture of the α- and β-forms. The value of 58° is therefore to be taken with caution. One other point remained to be considered, for trimethyl-β-methylxyloside prepared by the methylation of xylose in alkaline solution had a specific rotation some 10° lower than the correct value of −69.5° in chloroform. The similar observation of Carruthers and Hirst was thus confirmed and, recrystallization failing to improve the constant, the possibility remained that the two methods of alkylation had produced isomeric substances. On hydrolysis, however, the specimen with the incorrect specific rotation also gave trimethylxylose in 75% of the theoretical amount and the discrepancy was seen to be due to an impurity, possibly an isomeric form, which was difficult to remove. This observation should be of value when it is desired to prepare a methylated sugar in a state of optical purity by the aid of methyl sulfate and of alkali.

Experimental[9]

Preparation of Trimethyl-β-methylxyloside.—(a) A 5-g. portion of pure crystalline β-methylxyloside, $[\alpha]_D^{20}$ −65° in water, was methylated in the standard fashion with 40 g. of silver oxide and 25 cc. of methyl iodide, a little methyl alcohol being present in this first methylation only to dissolve the glucoside. Acetone was used to recover the product, which was then submitted to a second and a third treatment with the same reagents. The final separation of the trimethyl-β-methylxyloside from the inorganic residues was effected by extraction with ether, the yield of the crude, crystalline material after evaporation of the ether being 5.52 g. or 88% of the theoretical. After three recrystallizations from petroleum ether, cooled in ice and salt, the specific rotation in purified chloroform was $[\alpha]_D^{20}$ −69.6° (0.2439 g. in 25 cc. of $CHCl_3$ rotated the plane of polarization 1.36° to the left in a 2-dm. tube). This value was not appreciably changed by two further recrystallizations, the value found being $[\alpha]_D^{20}$ in $CHCl_3$, −69.5° (0.3669 g. in 25 cc. gave a rotation of −2.04° in a 2-dm. tube). The average of four sets of readings by two observers was $[\alpha]_D^{20}$ in $CHCl_3$, −69.5°. The rotation in water was $[\alpha]_D^{20}$ −81.7° (0.2463 g. in 25 cc. read −1.62° in a 2-dm. tube). The substance melted sharply at 51°. Estimation of methoxyl by Zeisel's method: 0.3144 g. gave 1.3968 g. of silver iodide, corresponding to 58.7% of OCH_3; calcd., 60.2. A subsequent

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[9] All methylations with silver oxide and methyl iodide were carried out in a round-bottomed flask equipped with an efficient water-cooled condenser, the two being united by a ground-glass joint in place of the customary rubber stopper. This innovation, while giving a product free from contamination by rubber and therefore more readily purified, required care in its use, as flask and condenser readily became cemented together.

larger-scale preparation (23 g.) after purification by several recrystallizations from ordinary absolute ether cooled in ice yielded substantially the same figures for the specific rotation, namely, −69.4° in $CHCl_3$ and −81.8° in H_2O.

(b) A 25-g. sample of carefully purified xylose was methylated as described by Carruthers and Hirst[4] first with methyl sulfate and alkali and then with 33 g. of silver oxide and 17 cc. of methyl iodide. The product crystallized on recovery from the latter process; yield, 20 g. or 64% of the theoretical. Once recrystallized from petroleum ether, 0.0684 g. dissolved in 25 cc. of chloroform and in a 2-dm. tube had an observed rotation of −0.34° and a specific rotation of −59.6°. A second recrystallization failed to change this value (0.1268 g. in 25 cc. of the same solvent had α −0.60° and $[\alpha]_D$ −59.0°). It is to be noted that the yield was only 64% as against 88% in (a), and likewise that the rotation is about 10° lower.

Preparation of Trimethyl-α-methylxyloside.—(c) Pure α-methylxyloside, prepared by the method of Bourquelot,[10] $[\alpha]_D$ +154.0° in water, was methylated with 60 g. of silver oxide and 37.5 cc. of methyl iodide for a 7.5-g. sample. Methyl alcohol (2.5 cc.) was also present, in this first methylation, to enable the xyloside to dissolve. Three such operations, however, failed to complete the methylation, as was evident when the liquid product was distilled, the refractive index varying with the fraction on which it was observed: methoxyl, found, 58.4%; theoretical, 60.2%. Accordingly, the total distillate of 7 g. was remethylated with 8 g. of silver oxide and 5 cc. of methyl iodide. After recovery it was dissolved in water and extracted with chloroform in order to remove most of the lower methylated impurities and the sirup obtained from the anhydrous chloroform extract was methylated for a fifth time. Evaporation at 80° (20 mm.) freed the trimethylmethylxyloside from solvent, the last traces of which were eliminated during the distillation, bath 110° (10 mm.). Rejecting the first six drops of the distillate, the seventh was found to have n_D^{24} 1.4391 and the last n_D^{25} 1.4387. Since data drawn from the work of Carruthers and Hirst show that the change in refractive index per degree rise in temperature is −0.00036° for a methylated xylose, the indices quoted are regarded as equivalent. In an estimation of methoxyl groups by Zeisel's method, 0.1151 g. gave 0.5208 g. of silver iodide; found: OCH_3, 59.7; calcd., OCH_3, 60.2.

In purified chloroform, $[\alpha]_D^{20}$ was +121.2°, 0.7273 g. having an observed rotation of 7.06° in 25 cc. of solution and in water +112.2°, values not appreciably changed by redistillation. After one redistillation $n_D^{22.6}$ of the fifteenth drop was 1.4398, that of the last, at 23°, 1.4397, while 0.4710 g. in 25 cc. of chloroform solution had α, 4.59° and $[\alpha]_D^{20}$ +121.7°. Trimethyl-α-methylxyloside, therefore, has a specific rotation in chloroform of the order of +121.5°. Similar measurements were made in water and in methyl alcohol; $[\alpha]_D^{20}$ in water was +112.7° (0.2942 g. in 25 cc. gave a rotation of 8.61° in a 2-dm. tube); $[\alpha]_D^{19}$ in CH_3OH was +122.2° (0.3791 g. in 25 cc. gave a rotation of +3.70° in a 2-dm. tube).

Preparation of Trimethyl-α-xylose.—(a) Pure trimethyl-β-methylxyloside, 6.29 g., dissolved in 120 cc. of 4% hydrochloric acid, was maintained at a temperature of 85°. The initial specific rotation of −73.1° increased, during seventy-five minutes, to a nearly constant value of +14.8°, whereupon the solution was neutralized with barium carbonate and filtered. In this preparation, trimethylxylose was isolated by a tedious extraction of the filtrate with large volumes of chloroform and by evaporation of the anhydrous extract to a sirup. A partial crystallization quickly occurred and the crystals were recrystallized from ice-cold ethyl acetate; yield, 2.3 g.; m. p. 91–92°; $[\alpha]_D$ +54.3° in chloroform. The original mother liquors, on standing at 0° for two days, deposited a further 1.2 g.; m. p. 88–91°; $[\alpha]_D$ +53.8° in chloroform, while further quantities

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[10] Bourquelot, *Ann. chim.*, 3, 298 (1915).

were obtained from the residual sirup on longer standing. Eventually the yield of crystalline trimethylxylose reached 85% of the theoretical. After two recrystallizations from ether, 0.5309 g. in 25 cc. of the chloroform solution had a rotation of 2.40° or $[\alpha]_D$ +56.4°. The third and fourth crystallizations raised this figure to $[\alpha]_D$ +58.0° (0.3223 g. in 25 cc. of chloroform had $\alpha = 1.50°$), a value which was not obtained when climatic conditions were hotter and more humid.

Mutarotation in Water.—0.2988 g. dissolved in 25.10 cc. had $\alpha = 0.55°$ twenty minutes after solution, while the equilibrium rotation of +0.43° was reached in three hours. The corresponding specific rotations are $[\alpha]_D$ +23° and $[\alpha]_D$ +17.9°, respectively.

(b) Recrystallized trimethyl-β-methylxyloside, $[\alpha]_D$ in $CHCl_3$ −59.6°, prepared by the direct methylation of xylose by methyl sulfate and alkali, was hydrolyzed under conditions similar to those detailed above. The specific rotation of the solution became practically constant at +16.2° and as this corresponds to an almost quantitative yield of trimethylxylose, the acid was neutralized with an excess of lead carbonate. Filtration removed the greater part of the inorganic salts from the well-cooled liquor and evaporation of the filtrate under diminished pressure left a dry residue from which hot ether readily extracted trimethylxylose. The sirupy product crystallized in stages when kept in the ice box for ten days, the final yield of crystalline material being 75% of the theoretical. Recrystallized from ether, the melting point was 90° and the mixed melting point with the specimen from (a) was 91–92°. Mutarotation occurred in chloroform, 0.4477 g. of the trimethylxylose in 25 cc. of solvent gave a reading of $\alpha = 1.99°$ or $[\alpha]^{20}_D$ +55.8°, falling in ninety minutes to the constant value $\alpha = 0.86°$ or $[\alpha]^{20}_D$ +24.2°, not changed by catalysis with a trace of acid. In water the first observation was made one minute after solution, 0.2392 g. in 25 cc. having $\alpha = 1.16°$, decreasing to the constant value of $\alpha = 0.34°$ in one hour. The corresponding specific rotations were $[\alpha]^{20}_D$ +62.8° and final $[\alpha]^{20}_D$ +17.6°.

(c) Liquid trimethyl-α-methylxyloside (2.48 g.) was dissolved in 4% hydrochloric acid and the volume increased to 50 cc. by addition of the same reagent. When maintained at 85° the specific rotation of the solution decreased from +109° to +19.4° in the course of 270 minutes. The yield of trimethylxylose, isolated as in (b), was 80% of that theoretically possible; m. p. 91–92°; mixed melting point with the two specimens obtained above, 91–92° in each case.

Mutarotation in Water.—0.2810 g. in 25 cc. of aqueous solution was read in a 2-dm. tube at 22°.

Minutes	0.5	2	3	4	5	8	13
$[\alpha]^{20}_D$	62.1	57.4	55.2	52.4	50.8	43.9	35.5
Minutes	21	24	34	48	88	123	180
$[\alpha]^{20}_D$	28.4	27.1	22.8	19.4	18.5	17.7	17.7

Extrapolation from these data gave a value of +64° for the initial specific rotation of trimethyl-α-xylose in water, while in a duplicate experiment +65° was the figure obtained.

The authors record their warm appreciation of the interest Dr. C. S. Hudson has taken in the work. One of them (C. B. P.) also wishes to thank the Commonwealth Fund of New York for the Fellowship which made his collaboration possible.

Summary

Trimethyl-α-methylxyloside has been prepared from pure crystalline α-methylxyloside. After purification by distillation its constants were n^{23}_D, 1.4397; $[\alpha]^{20}_D$ in $CHCl_3$, +121.5°; $[\alpha]^{20}_D$ in H_2O, +112.7; $[\alpha]^{20}_D$ in CH_3OH, +122.2.

Trimethyl-β-methylxyloside has been prepared in two ways: (a) from pure crystalline β-methylxyloside and (b) from pure xylose, using the methyl sulfate and sodium hydroxide method. After purification by recrystallization, the crystals resulting from (a) had the following constants: m. p. sharp at 51°; $[\alpha]_D^{20}$ in $CHCl_3$, −69.5°; $[\alpha]_D^{20}$ in H_2O, −81.7, while those resulting from (b) showed $[\alpha]_D^{20}$ in $CHCl_3$, −59.6°. As this value, which is about 10° low, did not change appreciably on recrystallization, it is concluded that this method gives a less pure product. On hydrolysis both trimethyl-α-methylxyloside and trimethyl-β-methylxyloside yield the same crystalline trimethylxylose. It is therefore concluded that these two substances contain the same ring structure, forming an α- and β-pair. They have thus been definitely correlated for the first time and likewise the parent substances, α- and β-methylxylosides, from which they were derived. The properties of the purified trimethyl-α-xylose were m. p. 91 to 92°; $[\alpha]_D^{20}$ in $CHCl_3$ (final), + 24.2; $[\alpha]_D^{20}$ in H_2O (initial), 64.5°; (final), 17.7°. It is to be noted that for the most part the constants given above differ quite materially from those previously recorded.

WASHINGTON, D. C.

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PROMOTER ACTION WITH OXIDE CATALYSTS FOR THE DECOMPOSITION OF ALCOHOLS[1]

BY HOMER ADKINS AND PAUL E. MILLINGTON

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It has been shown by experimental work described in a series of papers from this Laboratory[2] that the ratio of reaction products formed when alcohols are passed over solid catalysts is not primarily a function of the chemical nature of the catalyst mass but is determined by easily modifiable characteristics of the catalyst surface. Two explanations have been offered for this variation in the ratio of reaction products. Hugh Stott Taylor[3] in an extended discussion of our results among others stated that the oxides are dual catalysts, the metal part (metal ion) being dehydrogenating, and the oxygen part (oxide ions) being dehydrating. The ratio of the simultaneous reactions would then depend in part upon the ratio at the surface of active metal ions and active oxide ions. This latter ratio would depend upon the original distribution and upon the

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[1] The authors are indebted to E. I. du Pont de Nemours and Company for a fellowship held by Dr. Millington during the academic year 1927–1928.

[2] For references see Adkins and Lazier, THIS JOURNAL, **48,** 1671 (1926).

[3] Taylor, "Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York City, **1926,** Vol. IV, p. 25.