alizarin sulfonate were used as an indicator. The digestion did not involve a loss of time as compared with the usual Pregl method. The addition of a few drops of alcohol after decolorization seemed to be unnecessary with our modification. The digestion was complete after 40 minutes. Therefore, a little more than one hour was required for one estimation.

TABLE II

RESULTS IN MICRO-ANALYSES

	Substance	Wt., mg.	*N*/70 acid, cc.	Per cent. of nitrogen Found	Calcd.
1.	Nitrobenzoyl chloride.....	11.274	4.31	7.64	7.70
2.	β-Nitrosonaphthol.....	8.238	3.37	8.18	8.09
3.	Nitropropanol.....	9.152	6.20	13.49	13.33
4.	Picric acid.....	3.280	3.02	18.41	18.37
5.	*m*-Nitro-aniline.....	5.460	5.58	20.44	20.21
6.	Nitro-uracil.....	4.474	5.96	26.65	26.75

Excellent checks were obtained on dried samples, although in numbers 1,2 and 4 of Table II, samples were taken from stock bottles containing substances not labelled C. P. This fact might help to overcome the objection of industrial chemists to micro-analysis on account of the alleged danger in taking minute samples.

Summary

A micro Kjeldahl method is described which gives satisfactory results for the determination of nitrogen in nitro, azo and other similar compounds.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE][1]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XII.[2] THE PREPARATION AND PROPERTIES OF PURE ALPHA-METHYL *d*-LYXOSIDE

BY F. P. PHELPS AND C. S. HUDSON

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It was shown in Part VII[3] that the rotation of methyl-*d*-lyxoside which Van Ekenstein and Blanksma[4] have recorded ($[\alpha]_D = +40.2$ in water) is much smaller than the fairly concordant values that were calculated for the pure alpha form of this substance by three independent ways, namely, 66 (derived from the rotation of α-*d*-lyxose), 66 (from that of α-benzyl *d*-lyxoside), and 61 (from that of α-methyl *d*-xyloside). As

[1] Published by permission of the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] Part XI was published in THIS JOURNAL, **48**, 288 (1926).

[3] Hudson, *ibid.*, **47**, 272 (1925).

[4] Van Ekenstein and Blanksma, *Z. Ver. Deut. Zuckerind.*, **58**, 114 (1908).

they prepared less than a gram of the lyxoside and recrystallized it only once, there seemed a chance that the substance may not have been pure because experience indicates that the separation of the isomeric forms of the methyl glycosides often requires many recrystallizations, as was shown in the recent purification of the methyl arabinosides (Part VI).[5] Only by preparing the lyxoside in sufficient quantity to allow recrystallization to be repeated until the rotation reaches constancy can the reliability of the data be assured. Working with adequate quantities of methyl *d*-lyxoside prepared from *d*-lyxose (final $[\alpha]_D^{20} = -14$) and acidified methyl alcohol by Fischer's reaction, it has now been found that the pure substance shows a specific rotation $[\alpha]_D^{20} = +59.4$ in water. The crude lyxoside showed $[\alpha]_D^{20} = +45$ to $+50$. Since the yield is large it appears that the reaction produces principally the alpha form and in this respect resembles the similar condensation of mannose with methyl alcohol to α-methyl mannoside. It will be observed that the rotation +59.4 is near the calculated values previously mentioned, especially the one (+61) derived from α-methyl *d*-xyloside. One might conclude from this that α-methyl *d*-lyxoside is epimeric with α-methyl *d*-xyloside which is the assumption upon which the calculation was based. However, certain other comparisons of rotations lead the authors to believe that such is not the case and that α-methyl *d*-lyxoside does not possess the 1,5 ring which Hirst and Purves[6] have proved for methyl xyloside, but contains the 1,4 ring. The full discussion of this point will be deferred to a subsequent article as it is necessary to present first certain comparisons in the mannose and rhamnose series, soon to be published, from which certain pertinent coefficients will be obtained.

Pure *α-methyl d-lyxoside* crystallizes in colorless prisms which melt at 108–109° and sublime slowly in a high vacuum at 76°. It is odorless and very slightly sweet in taste, resembling methyl mannoside. It is readily soluble in water, methyl, ethyl and butyl alcohols and acetone, slightly soluble in hot, insoluble in cold, ether, very slightly soluble in hot chloroform and fairly soluble in hot ethyl acetate, from which it crystallizes well on cooling. Methoxyl determinations by the Zeisel method agree with the requirements of the formula $C_5H_9O_4.OCH_3$. Its specific rotations for several wave lengths of light are recorded in Table I.

Experimental Part

Following Van Ekenstein and Blanksma's directions, 1 g. of crystalline α-*d*-lyxose (final $[\alpha]_D^{20} = -14$) and 10 cc. of absolute methyl alcohol containing 0.5% of hydrogen chloride were heated in a sealed tube at 100° during two hours. The resulting dark colored solution was cooled, neutralized with silver carbonate, filtered and the filtrate was evaporated under reduced pressure to a thick sirup which was dissolved in twice

[5] Hudson, THIS JOURNAL, **47**, 265 (1925).

[6] *J. Chem. Soc.*, **123**, 1352 (1923).

its volume of ethyl acetate. Methyl lyxoside soon crystallized. The yield was 0.3 g. of crystals of $[\alpha]_D^{20} = +58$, and from the mother liquor 0.3 g. more of $[\alpha]_D^{20} = +42$.

In subsequent preparations on a larger scale Bourquelot's directions for making methyl glucoside[7] at the temperature of boiling methyl alcohol were followed with good results. This method proved to be much more convenient. A solution of 14 g. of pure crystalline α-*d*-lyxose in 195 cc. of absolute methyl alcohol containing about 1.5% of hydrogen chloride was refluxed for one hour, when it was found by Fehling's test that no free sugar remained. Boiling was continued for half an hour. The slightly yellow solution was cooled, neutralized with silver carbonate, decolorized by the addition of 3 g. of active carbon, filtered and the filtrate evaporated under reduced pressure to a thick sirup, which crystallized spontaneously and became solid when stirred. The mass was dissolved by heating it with about 5 cc. of absolute methyl alcohol. On the addition of four volumes of ethyl acetate crystallization took place almost at once and was complete after standing overnight at 8°; yield, 12 g.; $[\alpha]_D^{20} = +45$. The mother liquor was evaporated to dryness in a desiccator and yielded about 3 g. of amorphous material which has not crystallized. Methyl lyxoside may be recrystallized from water, methyl alcohol or ethyl acetate. The best results were obtained by dissolving the crystals in a little hot absolute methyl alcohol, adding an equal volume of warm absolute ethyl acetate, filtering with a little active carbon and adding several volumes of ethyl acetate, which causes rapid crystallization. The yield can be regulated by the relative proportions of methyl alcohol and ethyl acetate used. Moderate yields result in more rapid purification. After two such recrystallizations with yields of 50% each, the product reached a constant rotation ($[\alpha]_D^{20} = +59.4$ in water). By systematic crystallization there were finally obtained from 19 g. of lyxose 13 g. of methyl lyxoside of this rotation and about 5 g. of less pure crystals. In order to make certain that the substance was pure, this 13g. batch was then recrystallized five times in the way mentioned. The final product showed the same rotation. Its melting point was 108–109°, which is much higher than Van Ekenstein and Blanksma's value (80°).

Measurements of the rotation in aqueous solution were made with the large precision polariscope of this Bureau. The methyl lyxoside used was well ground and dried at 76° in a high vacuum. Some sublimation was noticed. All the readings recorded in the table are dextrorotations. The most accurate value (estimated as within 0.1%) is that for the mercury green line, λ = 546.1 mμ. The ratio of the rotations for the sodium yellow and mercury green lines, Rotation (λ = 589mμ)/Rotation (λ = 546.1 mμ) = 0.8497, is very near that for sucrose in aqueous solution (0.8492) and for quartz (0.85085).

TABLE I

ROTATION OF PURE ALPHA-METHYL *d*-LYXOSIDE IN AQUEOUS SOLUTION AT 20°

Concn.[a] G./100 cc.	Tube length Mm.	Sodium yellow λ = 589mμ α	Sodium yellow λ = 589mμ $[\alpha]_D^{20}$	Saccharimeter λ = approx. 585mμ Deg. S	Saccharimeter λ = approx. 585mμ $[\alpha]_S^{20}$	Mercury yellow λ = 578mμ α	Mercury yellow λ = 578mμ $[\alpha]_{578}^{20}$	Mercury green λ = 546.1mμ α	Mercury green λ = 546.1mμ $[\alpha]_{546.1}^{20}$	Mercury blue λ = 435mμ α	Mercury blue λ = 435mμ $[\alpha]_{435}^{20}$
5.0236	200	5.960	59.3	17.35	59.8	6.251	62.2	7.031	70.0	11.6	115
4.9624	200	5.917	59.6	17.05	59.5	6.105	61.5	6.923	69.8	11.8	119
4.1410	400	9.817	59.3	28.38	59.3	10.254	62.0	11.567	69.9	19.23	116
			Av. 59.4		59.5		61.9		69.9		117

[a] The concentration is expressed as grams of lyxoside per 100 cc. of the aqueous solution.

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

Two Zeisel estimations showed 18.79 and 18.95% of methoxyl group OCH_3 (0.3004 and 0.3154 g. of substance gave 0.4270 and 0.4529 g. of silver iodide); the formula $C_5H_9O_4.OCH_3$ (mol. wt. 164), requires 18.90%.

α-Methyl lyxoside is fairly easily hydrolyzed by acids. The reaction was found to follow the monomolecular order. The speed of hydrolysis in comparison with the speeds for several other carbohydrates, under the same conditions of acidity, temperature and concentration is recorded in Table II. Methyl lyxoside is hydrolyzed at 98° about five times as rapidly as methyl mannoside and about twice as rapidly as maltose. It is seen that at this temperature lactose is hydrolyzed more rapidly than maltose. Armstrong and Caldwell[8] found maltose to be hydrolyzed more rapidly than lactose at the lower temperature of 60.1° and inferred from the relative temperature coefficients of the hydrolysis of the two sugars that the rates would be equal at about 77° and that above this temperature lactose would hydrolyze faster than maltose. This predicted reversal of the relative speeds of hydrolysis is verified by the present measurements at 98°. Attention is called to the very slow rate of hydrolysis of α-methyl mannoside.

TABLE II

RATES OF HYDROLYSIS

Carbohydrate	Concn.[a] G./100 cc.	Acidity *M* HCl	*k*	Temp., °C.	Half period, min.
α-Methyl *d*-lyxoside	3	0.05	0.0041	98	74
Maltose	3	.05	.0019	98	158
Lactose	3	.05	.0024	98	125
Lactose	18	.05	.0032	98	94
α-Methyl *d*-mannoside	3	.5	.0089	98	34
α-Methyl *d*-mannoside	3	.05	.00089[b]	98	339

[a] The concentration of carbohydrate is expressed as g. of anhydrous substance per 100 cc. of solution; that of acid as moles per liter of solution; thus the maltose solution contained at 20° 30 g. of maltose ($C_{12}H_{22}O_{11}$) and (0.05) (36.5) = 1.825 g. of HCl per liter. The rate is expressed as the monomolecular velocity-coefficient $k = \frac{1}{t} \log_{10} \frac{r_0 - r_\infty}{r - r_\infty}$, r_0 and r_∞ being the initial and final rotations and r the rotation at t minutes from the start. The half period is the time in minutes required for the hydrolysis to be half complete.

[b] This value for 0.05 *M* acid was not directly measured but was calculated from the value for 0.5 *M* HCl on the assumption that the rate is directly proportional to the acidity.

Summary

Pure α-methyl *d*-lyxoside has been prepared and its rotation ($[\alpha]_D^{20}$ = +59.4 in water) found to agree fairly well with previously calculated values (61 to 66). Its rate of hydrolysis by acid has been measured and compared with the rates of several other carbohydrates under similar

[8] Armstrong and Caldwell, *Proc. Roy. Soc.* (London) **73**, 530 (1904).

conditions. The reversal of the relative speeds of hydrolysis of lactose and maltose that was predicted by E. F. Armstrong and Caldwell has been realized.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

ORGANIC BISMUTH COMPOUNDS. I. PREPARATION OF TRICARBOXY-TRIPHENYLBISMUTH DICHLORIDES AND CERTAIN NITRO-TRIARYL BISMUTH COMPOUNDS

BY J. V. SUPNIEWSKI AND ROGER ADAMS

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During the past few years the administration of bismuth in one form or another in place of, or along with organic arsenic compounds in the treatment of spirochetosis has become quite frequent practice. The compounds most used are bismuthates formed from sodium potassium tartrate, gallic acid, pyrogallol, iodogallic acid, iodoquinine and other substances of less importance, the first one being in most general use; in all of these, bismuth is not attached to carbon but is in salt-like formation, and the compounds frequently have variable chemical composition and physical properties depending on the mode of preparation. Colloidal preparations of bismuth and bismuth oxide have also been used in practice.

The success in chemotherapy of organic arsenic compounds where arsenic is attached to carbon leads to the conclusion that among organic bismuth compounds where bismuth is attached to carbon might be found pure substances of low enough toxicity and high enough therapeutic action to replace the bismuth salts[1] used at present. Only one or two attempts to use true organic compounds of bismuth in chemotherapy have been reported. Giesma[2] obtained favorable results toward trypanosomes and spirochetes by the intramuscular injection of triphenyl bismuth in oil suspension or by percutaneous treatment. The object of this research has been the synthesis and study of various new organic bismuth compounds; the possibility of water-soluble carbon-bismuth compounds has been kept especially in mind.

All the compounds of the types R_3Bi, R_2BiX, $RBiX_2$, where R is aliphatic and X is halogen, are very unstable and in many cases spontaneously inflammable. Moisture causes the decomposition of most of them. No compounds of the above types where one R is aliphatic and the others aromatic have been prepared although many attempts are described; the products are always triaryl bismuthine and traces of trialkyl bismuthine. Compounds R_2BiX and $RBiX_2$ where R is aromatic and X halogen

[1] Kolle, *Medizin. Klinik*, **20**, 1097 (1923).

[2] Giesma, *Dermatol. Wochenschr.*, **76**, 523 (1923); *Münch. med. Wochschr.*, **79**, 1452 (1923).