scribed by Dische[21]; 2.5×10^{-4} *M* 2-amino-2-deoxy-D-xylose hydrochloride (A, Fig. 2), 7.5×10^{-4} *M* 2-amino-2-deoxy-D-glucose hydrochloride (B), 7.5×10^{-4} *M* 2-amino-2-deoxy-D-galactose hydrochloride (C), 8.6×10^{-4} *M* 2-amino-2-deoxy-L-pentose hydrochloride (VI) (D), 6.5×10^{-4} *M* 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (E) and 8.9×10^{-4} *M* D-glucose (F). The light absorption properties of the resulting cherry-red solutions were measured in a Cary, model 10, recording spectrophotometer,[28] within the wave length range of 400–550 mμ. The data obtained are presented in Fig. 2.

2-Acetamido-2-deoxy-L-pentose.—A solution of 0.3 g. of the 2-amino-2-deoxy-L-pentose hydrochloride in 3 ml. of methanol was treated with 0.25 g. of silver acetate and 0.3 ml. of acetic anhydride and the mixture was left at 0° for 18 hr. and at 25° for 5 hr. It was then filtered and the filtrate was treated with 3 ml. of 0.1 *N* hydrochloric acid for 2 hr. and refiltered. The solution was concentrated to a sirup which was dissolved in abs. ethanol and deionized with Amberlite MB-1. The deionized solution and the washings were concentrated to 10 ml. and then ether was added to incipient turbidity. The resulting product of 2-acetamido-2-deoxy-L-pentose was recrystallized from a mixture of ethanol and ether; yield 15 mg., m.p. 115–123°.

Anal. Calcd. for $C_7H_{13}NO_4$: C, 43.98; H, 6.85; N, 7.32. Found: C, 44.12; H, 7.03; N, 7.78.

COLUMBUS 10, OHIO

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[28] Made by Applied Physics Corp., Pasadena, Calif.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

Uronic Acid Fragments from Slash Pine (*Pinus elliottii*) and their Behavior in Alkaline Solution[1,2]

BY ROY L. WHISTLER AND G. N. RICHARDS

RECEIVED APRIL 24, 1958

4-*O*-Methyl-D-glucuronic acid is identified as the major acidic component of the hemicellulose fraction of slash pine. Other uronic acids are not present in more than trace amounts. The predominant mode of linkage of the uronic acid is indicated by the isolation of the aldobiouronic acid, 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-α-D-xylose in high yield, but the presence of a complex mixture of other acidic oligosaccharides suggests that other types of linkage may also be present to a small extent. The resistance of glycosides derived from uronic acids toward acidic hydrolysis is discussed. The action of lime-water on 4-*O*-methyl-D-glucuronic acid follows a similar course to that previously observed with 4-*O*-methyl-D-glucose and yields a dibasic acid analogous to the monobasic D-gluco*iso*saccharinic acid. The aldobiouronic acid in lime-water yields no further acids.

As a preliminary step to the examination of the polysaccharide components of slash pine, examination was made of the acidic fragments produced by acidic hydrolysis of the whole hemicellulose-B fraction. This hemicellulose fraction is prepared by alkaline extraction[3] of holocellulose and is subject to partial hydrolysis with sulfuric acid. During acid treatment the separation of a water-insoluble polysaccharide results from rapid hydrolysis of solubilizing side-chains as observed previously[4] with birch wood hemicellulose. Isolation of the acidic fragments from the hydrolysis mixture is effected by a strongly basic polystyrene resin in the carbonate form.[5] There is thus reasonable certainty of complete uptake of all acids, including stable lactones which may form, and of their complete recovery on elution. This separation procedure also tends to avoid alkaline degradation or rearrangement of neutral sugars.

Analysis of the acidic products on a cellulose column yields fractions shown in Table I. Each fraction gives only a single spot on paper chromatography, but results of further hydrolysis and subsequent examination of the minor fractions (3, 4 and 5) indicate that they are probably mixtures. On further hydrolysis each fraction yields chromatographic evidence that 4-*O*-methyl-D-glucuronic acid is the major acidic component and there is tentative evidence of traces of galacturonic acid. The major fractions (1 and 2) are 4-*O*-methyl-D-glucuronic acid (I) and 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose (II), respectively. 4-*O*-Methyl-D-glucuronic acid is obtained as its brucine salt and this appears to be the first simple crystalline derivative of the acid to be reported.

4-*O*-Methyl-D-glucuronic acid also is found as the predominant acidic component of other soft woods[6] such as poplars[7,8] and Scots pine.[9] Some of these woods also yield the same 1→2-linked aldobiouronic acid as observed in slash pine.

TABLE I

ACIDS FROM HYDROLYSIS OF HEMICELLULOSE-B

Fraction	Yield from hemicellulose, %	$[\alpha]^{25}D$ in water	R_x (solvent A)
1	0.9	+47°	1.48
2	3.9	+94	0.75
3	0.2	+61	.47
4	.5	+55	.31
5	.2	+45	.24

The aldotriouronic acid previously isolated[10] from slash pine must almost certainly have contained the same aldobiouronic acid unit (II), although in the present work the aldotriouronic acid was not produced in more than trace amount.

The ease of isolation of aldobiouronic acids and their resistance to further hydrolysis have often

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[1] Presented before the Division of Cellulose Chemistry at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[2] Journal Paper No. 1272 of the Purdue University Agricultural Experiment Station, Lafayette, Ind.

[3] R. L. Whistler, J. Bachrach and D. R. Bowan, *Arch. Biochem.*, **19**, 25 (1948).

[4] A. P. Yundt, THIS JOURNAL, **71**, 757 (1949).

[5] G. Machell, *J. Chem. Soc.*, 3389 (1957).

[6] J. Saarnio, K. Wathen and C. Gustafsson, *Paperi ja Puu*, **36**, 209 (1954).

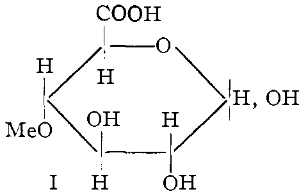
[7] P. A. J. Gorin, *Can. J. Chem.*, **35**, 595 (1957).

[8] J. K. N. Jones and L. Wise, *J. Chem. Soc.*, 3389 (1952).

[9] A. R. M. Gorrod and J. K. N. Jones, *ibid.*, 2522 (1954).

[10] E. Anderson, J. Kesselman and E. C. Bennett, *J. Biol. Chem.*, **140**, 563 (1941).

received comment,[11] but the logical conclusion that the presence of the carboxylic acid group causes stabilization of the adjacent glycosidic linkage has not been verified quantitatively. Hence the hydrolysis constant of 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose (II) in normal sulfuric acid at 95° is determined here, by measurement of the rate of formation of xylose. The results (Table II) show an apparent progressive fall in rate of xylose formation, but probably this is due to loss of xylose by acidic degradation and perhaps to some extent to recombination of xylose and uronic acid ("reversion"). It is assumed that the initial value approximates to the true hydrolysis constant for these conditions. For comparison the approximate hydrolysis constant of the neutral disaccharide (III) resulting from reduction of the aldobiouronic acid (II) was calculated from the rate of change of optical rotation under the same hydrolysis conditions. Maltose also was treated in the same way (Table III).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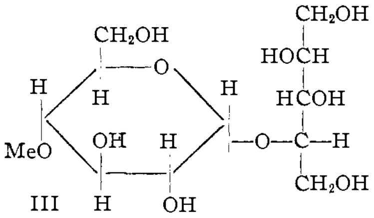

III

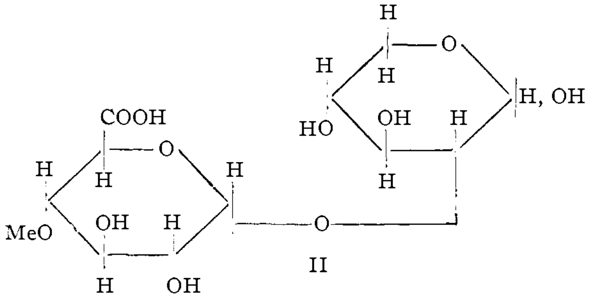

II

TABLE II

HYDROLYSIS OF 2-*O*-(4-*O*-METHYL-α-D-GLUCOPYRANOSYLURONIC ACID)-D-XYLOSE IN 1.07 *N* SULFURIC ACID AT *ca.* 95°

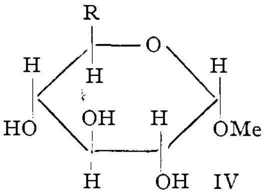
Time, hr.	Xylose produced, mmole.	Hydrolysis, %	$k \times 10^{-4}$, min.$^{-1}$
1.0	0.0220	7.4	5.7
2.0	.0407	13.7	5.3
3.0	.0543	18.3	4.2
5.0	.0777	26.1	3.8

TABLE III

HYDROLYSIS CONSTANTS OF ACIDIC AND NEUTRAL α-D-GLUCOSYL DISACCHARIDES

Disaccharide	k ($\log_{10}$, min.$^{-1}$)
2-*O*-(4-*O*-Methyl-α-D-glucopyranosyluronic acid)-D-xylose (II)	5.7×10^{-4}
2-*O*-(4-*O*-Methyl-α-D-glucopyranosyl)-D-xylitol (III)	1.0×10^{-2}
4-*O*-(α-D-Glucopyranosyl)-D-glucose (maltose)	1.09×10^{-2}

Results indicate that the glycosidic linkage is rendered more stable to acidic hydrolysis by the presence of the carboxyl group in the glycosidic moiety. Foster and Overend[12] have previously discussed the decrease in ease of hydrolysis in glycosides of general type IV with increase in bulk of the group R. They interpreted this effect in terms of non-bonded interaction of R during changes in conformation of the pyranose ring during hydrolysis. The differences shown in Table III are due at least in part to the same effect since the carboxyl group is more bulky than the hydroxymethyl. However, a comparison of the relative rates of hydrolysis of heptopyranosides (IV, R = $CH_2OH \cdot CH(OH)-$) and the corresponding hexopyranosides (IV, R = $-CH_2OH$)[13] shows only a two- or threefold difference, compared with about a twenty-fold difference between II (R = $-COOH$) and maltose (III, R = $-CH_2OH$), although the change in bulk of R is probably similar in the two cases. Any differences in Table III due to the 4-*O*-methyl group or to the aglycon group are likely to be relatively small. Therefore it seems probable that the inductive effect of the carboxyl group also has a significant stabilizing effect on the glycosidic linkage. This agrees with previous observations of stabilization of the glycosidic linkage by substitution of the sugar ring with other electrophilic groups such as *p*-toluenesulfonyl esters[14] and halogens,[15] and possibly also with the resistance of periodate oxidation products toward hydrolysis.[16]


IV

The action of alkali on 4-*O*-methyl-D-glucuronic acid (I) is also examined in view of its possibility as a model compound for alkaline degradation of carboxylic polysaccharides. The acid apparently reacts smoothly with lime-water at 25°, but measurement of the rate of reaction is vitiated by separation of a calcium salt during the reaction. The acid yield, however, corresponds to the formation of one equivalent of a new acidic group, and a crystalline brucine salt of the product is obtained, whose elemental analysis corresponds to the dibasic salt of the dicarboxylic acid (V). It is concluded therefore that the reaction follows the anticipated course shown, which is analogous to the similar reaction of 4-*O*-methyl-D-glucose.[17]

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[11] *E.g.*, W. Pigman, "The Carbohydrates," Academic Press, Inc., New York, N. Y., 1957, p. 319.

[12] A. B. Foster and G. W. Overend, *Chemistry & Industry*, 566 (1955).

[13] H. S. Isbell and H. L. Frush, *J. Research Natl. Bur. Standards*, **24**, 125 (1940); ref. 11, p. 209.

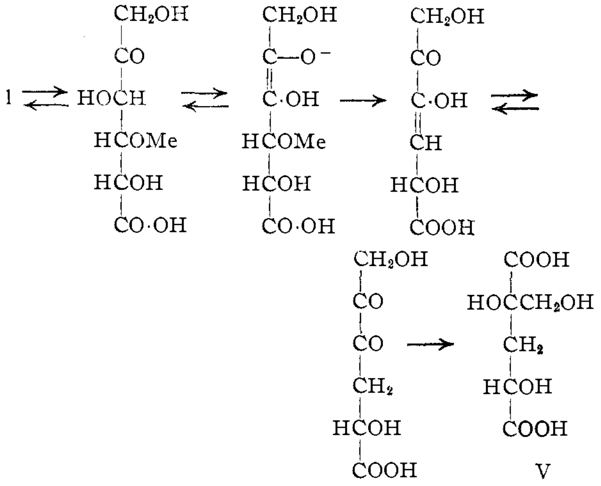
[14] J. K. L. Jones and W. H. Nicholson, *J. Chem. Soc.*, 3050 (1955).

[15] F. H. Newth, W. G. Overend and L. F. Wiggins, *ibid.*, 10 (1947).

[16] *Cf.* G. N. Richards, *ibid.*, 3222 (1957).

[17] J. Kenner and G. N. Richards, *J. Chem. Soc.*, 1810 (1955).

Action of lime-water at 25° on the aldobiouronic acid II produced no increase in acidity after 48 hours. This behavior is in accordance with observations on another 1→2-linked disaccharide[18] and


V

also with 2,3-di-*O*-methyl-D-glucose,[19] and is regarded as characteristic of 2-*O*-substituted reducing sugars.

Experimental

Paper Chromatography.—Separations were made on Whatman No. 1 filter paper, unless otherwise stated, at 25° using these various solvents and sprays: solvent A, ethyl acetate–acetic acid–formic acid–water (18:3:1:4, v./v.); solvent B, ethyl acetate–pyridine–water (40:11:6, v./v.). Spray A, aniline hydrogen phthalate[20]; spray B, B. D. H. 4.5 indicator[21]; spray C, sodium metaperiodate–potassium permanganate[22]; spray D, hydroxylamine–ferric chloride[23]; R_x = rate of movement relative to D-xylose.

Hemicellulose-B.—Fresh slash pine (*Pinus elliottii*) wood was freed from bark, planed and the planings passed through a Wiley mill. The ground wood was extracted continuously for 24 hours in a Soxhlet apparatus with ethanol-benzene (1:2, v./v.) and the resulting extractive-free, air-dried wood was delignified by treatment with sodium chlorite under the conditions described earlier.[3] The holocellulose was washed with acetone, air-dried (recovery 72%), extracted with 10% potassium hydroxide solution and hemicellulose-A and -B fractions obtained.[3] The B-fraction was washed several times with ethanol, dried over calcium chloride and used without further purification.

Partial Hydrolysis of Hemicellulose-B.—A 250-g. portion of air-dried hemicellulose was stirred in 2.5 l. of water at 90–95° for 18 hours, 625 ml. of 20% sulfuric acid was then added and heating and stirring continued for a further 7 hours. During this time a white precipitate separated. The mixture was filtered, adjusted to *p*H 3–4 with aqueous barium hydroxide and finally neutralized with barium carbonate. The filtrate was passed through 200 ml. of Amberlite resin IR-120 (H) and then stirred with 300-ml. of Amberlite resin IRA-400 (carbonate form[5]) for 20 hours at room temperature. The resin was washed in a column with 20 l. of water until the washings were free from reducing sugars. It was then stirred with 600 ml. of 1 *N* sulfuric acid, further eluted in a column with 400 ml. of 1 *N* sulfuric acid and finally washed with 2 l. of water. Combined acidic eluates and washings were neutralized with barium hydroxide solution followed by barium carbonate as above, filtered, passed through 200 ml. of Amberlite resin IR-120 (H) and evaporated to a thick sirup (24.90 g.). Chromatography in solvent A, spray A, indicated a main component of R_x 0.77, with other components of R_x 1.48, 0.47, 0.31, 0.24 with streaking to the origin.

Chromatographic Analysis of Uronic Acids.—A 4.32-g. portion of the sirup from the previous experiment was transferred to a cellulose column (5 cm. diameter, 50 cm. long) and eluted with a mixture of ethyl acetate, acetic acid and water (9:2:2, v./v.). The effluent was collected in 50-ml. fractions which were examined for optical rotation and suitable samples were concentrated for paper chromatography. Relevant fractions were evaporated to dryness, distilled with water until free from acetic acid, and the dried residues extracted with a mixture of methanol and acetone (1:1, v./v.). Evaporation of the extracts yielded the fractions shown in Table I. Intermediate fractions containing small amounts of 2 and 3, and 4 and 5, were rejected.

4-*O*-Methyl-D-glucuronic Acid.—A 0.2-g. portion of fraction I was boiled with 5% hydrochloric acid in 20 ml. of dry methanol, reduced with lithium aluminum hydride and hydrolyzed by methods described earlier.[24] The product yielded 4-*O*-methyl-D-glucose phenylosazone when treated with phenylhydrazine in aqueous acetic acid in the usual manner, and when recrystallized from benzene this showed m.p. 154–157°, alone or in admixture with an authentic sample.

A further sample of fraction I was treated with excess brucine and water at 100° for 5 minutes and the brucine salt isolated in the usual way. Brucine 4-*O*-methyl-D-glucuronate crystallized from aqueous ethanol as fine needles, m.p. 168–169°, $[\alpha]^{25}\text{D}$ −9.6 ± 0.2° (*c* 5, water).

Anal. Calcd. for $C_{30}H_{38}O_{11}N_2$: C, 59.8; H, 6.4; N, 4.6. Found: C, 60.0; H, 6.6; N, 4.4.

2-*O*-(4-*O*-Methyl-α-D-glucopyranosyluronic Acid)-D-xylose.—A 0.25-g. portion of fraction II was methylated with diazomethane and the ester subsequently reduced with sodium borohydride[7] to yield 0.20 g. of 2-*O*-(4-*O*-methyl-α-D-glucopyranosyl)-D-xylitol, $[\alpha]^{25}\text{D}$ + 81° (*c* 1, water). Gorin[7] reports $[\alpha]^{27}\text{D}$ +86°. Paper chromatography in solvent B, spray B, showed only one component (R_{glucose} 0.94), but acetylation yielded an amorphous product. A solution containing 0.04 g. of xylitol derivative in 10 ml. of 1.07 *N* sulfuric acid, when heated on the steam-bath, showed the following changes in optical rotation (25°, 1-dm. tube): α° + 0.33° (initial), 0.26° (0.25 hour), 0.22° (0.5 hour), 0.16° (1.0 hour), 0.13° (2.0 hours), 0.12° (3.0 hours), 0.11° (5.0 hours). The solution was next neutralized with barium carbonate, filtered and evaporated to dryness. The residue, when treated with phenylhydrazine in 15% acetic acid at 100° for 30 min., yielded 4-*O*-methyl-D-glucose phenylosazone, showing m.p. and mixed m.p. 153–157° after one recrystallization from benzene.

A further 1.728-g. portion of fraction II was methylated with dimethyl sulfate and sodium hydroxide solution as described earlier.[24] The methylated product was a colorless sirup (1.60 g.) which was dissolved in ether and esterified by addition of excess ethereal diazomethane solution. The resulting solution was concentrated and then reduced by addition of an ethereal solution of lithium aluminum hydride,[24] yielding 1.31 g. of a colorless sirupy product. This was further methylated[25] in 20 ml. of dioxane solution by stirring with 6.5 g. of powdered sodium hydroxide at 45° while dimethyl sulfate (8.5 ml.) was added dropwise during 1 hour. The temperature was raised to 60° and stirring continued for a further 5 hours. After stirring at room temperature overnight the mixture was filtered, the salts washed with benzene and the combined filtrate and washings evaporated to 1.00 g. of a colorless sirup.

A solution of this product in 20 ml. of 1.07 *N* sulfuric acid, when heated on the steam-bath, showed the following changes in $[\alpha]^{25}\text{D}$: +80.6° (initial), +77.6° (0.5 hour), +53.4° (2.5 hours), +47.8° (3.5 hours), +44.2° (4.5 hours), +44.0° (5.5 hours). The solution was neutralized with barium carbonate and the products separated and isolated as described earlier.[24] In this way 2,3,4,6-tetra-*O*-methyl-D-glucose (0.410 g.) was obtained with m.p. and mixed m.p. 88–90°, $[\alpha]^{25}\text{D}$ +82 ± 2° (*c* 0.5, water) after recrystallization from hexane. 3,4-Di-*O*-methyl-D-xylose was

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[18] R. L. Whistler and W. M. Corbett, This Journal, **77**, 3822 (1955).

[19] J. Kenner and G. N. Richards, *J. Chem. Soc.*, 2921 (1956).

[20] S. M. Partridge, *Nature*, **164**, 443 (1949).

[21] British Drug Houses indicator described by K. K. Nair and P. T. Muthe, *Naturwiss.*, **43**, 106 (1956).

[22] R. U. Lemieux and H. F. Bauer, *Anal. Chem.*, **26**, 920 (1954).

[23] M. Abdel-Akher and F. Smith, This Journal, **73**, 5859 (1951).

[24] R. L. Whistler, H. E. Conrad and L. Hough, *ibid.*, **76**, 1668 (1954).

[25] B. Lindberg and B. Wickberg, *Acta Chem. Scand.*, **8**, 569 (1954).

obtained in a yield of 0.276 g. as a sirup and oxidized by bromine in presence of barium carbonate to yield 3,4-di-*O*-methyl-D-xylono-δ-lactone with m.p. and mixed m.p. 65–67°, $[\alpha]^{25}D$ $-51°$ (10 min.) → $-21°$ (48 hours, *c* 2, water), after recrystallization from ether.

Further Examination of Fractions III, IV and V.—Five-mg. samples of fractions III, IV and V were heated at 100° with 1-ml. portions of 1 *N* sulfuric acid for 16 hours, then neutralized with barium carbonate, filtered and shaken with Amberlite resin IRA-45(OH). Paper chromatography in solvent B, spray A, then indicated xylose as the major neutral product from each fraction. In addition, components corresponding to the following sugars also were detected in much smaller amounts; III, galactose (R_x 0.43) and mannose (R_x 0.67); IV, galactose, glucose (R_x 0.54), mannose and rhamnose (R_x 1.44); V, galactose, glucose and mannose.

Further samples of III, IV and V were esterified, reduced and hydrolyzed as described earlier[24] and the products examined by paper chromatography in solvent B. Components corresponding to the following sugars were detected and the approximate relative amounts are given; III, galactose, xylose, 4-*O*-methylglucose (R_x 1.20) (1:1:1); IV, galactose, xylose, 4-*O*-methylglucose, rhamnose, glucose, mannose (3:5:2:1:trace:trace); V, galactose, glucose, xylose, 4-*O*-methylglucose (1:1:3:2).

Hydrolysis Constant of 2-*O*-(4-*O*-Methyl-D-glucopyranosyluronic Acid)-D-xylose.—A solution of 0.1010 g. of aldobiouronic acid in 20 ml. of 1.07 *N* sulfuric acid was heated on the steam-bath under reflux. At intervals the solution was cooled and 2-ml. samples added to a mixture of Amberlite resin IRA-400 (5 ml., carbonate form) and 10 ml. of water and stirred for 3 hours. The solution was filtered, and the resin washed with water until the combined filtrate and washings totaled 50 ml. The xylose present in this solution was determined by the ferricyanide method[26] and the results are shown in Table II, the "constant" being calculated from the expression $k = 1/t \times \log C_0/C_t$.

Hydrolysis Constant of Maltose.—A solution of 0.2467 g. of maltose monohydrate in 50 ml. of 1.07 *N* sulfuric acid was heated under reflux on the steam-bath and the following changes in $[\alpha]^{25}D$ observed: +107° (15 min.), +90° (30 min.), +77° (45 min.). Using the expression

$$k = 1/t \times \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

the mean value for the hydrolysis constant is $k = 1.09 \times 10^{-2}$ min.$^{-1}$.

Action of Lime-water on 4-*O*-Methyl-D-glucuronic Acid.—A solution containing 0.142 g. of the acid in 50 ml. of oxygen-free 0.04 *N* lime-water was kept at 25° for 10 days. During this time a white precipitate separated and the solution became non-reducing to Fehling solution. Amberlite resin IR-120(H) (10 ml.) was added and the mixture shaken for 10 min. to break down and dissolve the calcium salt. The solution was then filtered and the resin washed with water. Titration with alkali of an aliquot of the combined filtrate and washings indicated the presence of 1.39 meq. of acid (2.04 equiv./mole starting material). The neutralized aliquot was again treated with Amberlite resin IR-120(H), combined with the remainder of the acid solution and evaporated to 0.130 g. of a colorless sirup. Paper chromatography of this product in solvent A showed an acid spot (R_x 1.12) (sprays B and C) and an elongated zone (approx. R_x 2.1) which gave a weak lactone reaction (spray D) and probably corresponded to monolactones of the dibasic acid.

The above product was combined with material from a similar reaction (total 0.230 g.) and heated 4 hours on the steam-bath with water and excess brucine. The mixture was cooled, filtered, washed twice with chloroform and concentrated to about 10 ml. On standing at 0° for 18 hours 0.148 g. of crystals separated and when recrystallized from aqueous acetone showed m.p. 189–194°, $[\alpha]^{25}D$ $-29.3 \pm 0.5°$ (*c* 2, 50% aqueous ethanol).

Anal. Calcd. for $C_{52}H_{62}O_{15}N_4$: C, 63.5; H, 6.4; N, 5.7. Found: C, 63.1; H, 6.4; N, 5.4.

Mother liquors from the original crystallization were evaporated to a colorless sirup (0.738 g.) and retreated with brucine as above to yield a further quantity (0.31 g.) of the same brucine salt.

Action of Lime-water on 2-*O*-(4-*O*-Methyl-D-glucopyranosyluronic Acid)-D-xylose.—A solution containing 0.0776 g. of the disaccharide in 25 ml. of oxygen-free 0.039 *N* lime-water was kept at 25° and at intervals aliquots were added to excess hydrochloric acid and back titrated with sodium hydroxide. These acid yields were obtained: 1.01 (0.05 hour), 0.995 (24 hours), 1.00 (48 hours) equiv./mole.

LAFAYETTE, IND.

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(26) H. C. Hagedorn and B. N. Jensen, *Biochem. Z.*, **135**, 46 (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

Bis-(β-Diketones). I. Synthesis of Compounds of the Type $RCOCH_2CO–Y–COCH_2COR$[1,2]

BY DEAN F. MARTIN, MAURICE SHAMMA AND W. CONARD FERNELIUS

RECEIVED APRIL 7, 1958

A number of new bis-(β-diketones) of the type $RCOCH_2CO–Y–COCH_2COR$ have been prepared: R = C_6H_5, Y = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$, $(CH_2)_7$, 1,3-C_6H_4, 1,4-C_6H_4 and 4,4′-$C_6H_4 \cdot C_6H_4$; R = *p*-$CH_3OC_6H_4$, Y = 1,4-C_6H_4; R = $CH_2{=}CHCH_2CH_2$, Y = 1,3-C_6H_4 and $(CH_2)_8$. The first two were prepared by the condensation of a bis-(acyl chloride) with the sodium salt of a ketone and the remainder by Claisen condensations. The infrared and ultraviolet absorption spectra indicate that these bis-(β-diketones) exist predominantly in the enolic form both in the solid state and in 95% ethanol.

Introduction

In continuation of an investigation into the chelation behavior of bis-(β-diketones),[3] several new compounds of the type $RCOCH_2CO–Y–COCH_2COR$ have been prepared. Previous investigators have reported the synthesis of the compounds where Y = nothing, R = CH_3[4]; R = C_2H_5[5]; R = C_6H_5[6]; R = 2,4-$(CH_3)_2C_6H_3$ and R = 4-$CH_3OC_6H_4$[7]; Y = $(CH_2)_2$, R = C_6H_5[8]; Y = $(CH_2)_3$, R = C_6H_5[9]; Y = $(CH_2)_8$, R = CH_3 and C_6H_5[3]; Y = 1,4-C_6H_4, R = CH_3[10]; and Y = 1,5-[2,4-$(CH_3O)_2C_6H_2$], R = CH_3, $C_6H_5CH_2$ and 4-$CH_3OC_6H_4$.[11] There are reported

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(1) This research was supported in whole by the United States Air Force under Contract AF33(616)-2742, monitored by the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio.

(2) Based upon a portion of the doctoral dissertation of Dean F. Martin, The Pennsylvania State University, 1958.

(3) E. H. Holst, Ph.D. dissertation, The Pennsylvania State University, 1955.

(4) L. Claisen and N. Stylos, *Ber.*, **21**, 1141 (1888).

(5) O. Diels, J. Sielisch and E. Müller, *ibid.*, **39**, 1328 (1906).

(6) E. Brôme and L. Claisen, *ibid.*, **21**, 1131 (1888).

(7) O. Widman and E. Virgin, *ibid.*, **42**, 2794 (1909).

(8) G. H. Daub and W. S. Johnson, THIS JOURNAL, **72**, 501 (1950).

(9) H. Wieland and I. Drishaus, *Ann.*, **474**, 102 (1929).

(10) L. Berend and P. Herms, *J. prakt. Chem.*, [2] **74**, 131 (1906).

(11) J. Algar, *Proc. Roy. Irish Acad.*, **33B**, 86 (1916); *C. A.*, **10**, 2577 (1916).