EXPERIMENTAL[9]

Finely ground *Kuhnia eupatorioides* L. var. *pyramidalis*, collected near Tallahassee in summer 1958, wt. 3.2 kg., was extracted with chloroform in a Soxhlet extractor for 2 days. The solvent was removed. The residue was taken up in 800 ml. of hot ethanol and diluted with 900 ml. of hot water containing 25 g. of lead acetate and 5 ml. of acetic acid. After 1 day the mixture was filtered, the brown filtrate was concentrated at reduced pressure and then extracted thoroughly with chloroform. Drying followed by removal of chloroform yielded 31 g. of viscous gum which could not be induced to crystallize.

The major part, 25 g., was taken up in benzene and chromatographed over 300 g. of alumina (Alcoa Grade F-20). Fractions 1–7 (150 ml. each of benzene) eluted a trace of oil, fractions 8–23 (150 ml. each of chloroform) eluted gum containing crystalline material as did fraction 24 (1.5 l. of 9:1 chloroform-methanol). On trituration with a small amount of ether, the gum dissolved, leaving a total of 1.1 g. of crystalline material from fractions 8–24. Repeated recrystallization from acetone-ether yielded 0.42 g. of yellow needles of artemetin, m.p. 158–159°, lit.159°,[5] 161.5,[7] 163–164°,[6] olive-green color with alcoholic ferric chloride solution, intense yellow color with alcoholic potassium hydroxide and cond. sulfuric acid, salmon-pink color on treatment with magnesium and hydrochloric acid.

Anal. Calcd. for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19; $-OCH_3$, 38.37. Found: C, 61.86; H, 5.25, $-OCH_3$, 38.03.

A solution of 0.07 g. of the flavone in 1 ml. of pyridine was treated with 0.5 ml. of acetic anhydride, warmed on the steam bath for one hour and allowed to stand overnight. Dilution with water followed by two recrystallizations from methanol–methylene chloride yielded colorless fluffy needles of 5-acetoxy-3,6,7,3′,4′-pentamethoxyflavone, m.p. 160.5–161.5°, lit.[6] 162–163°. The procedure recommended by Mazur and Meisels[6] gave impure material.

Anal. Calcd. for $C_{22}H_{22}O_9$: C, 61.39; H, 5.15. Found: C, 61.24; H, 5.08.

A solution of 0.14 g. of the flavone in 15 ml. of acetone was treated with 0.5 ml. of dimethyl sulfate and 5 ml. of 15% potassium hydroxide solution and allowed to stand for 12 hr. with occasional shaking. Dilution with water followed recrystallizations from acetone-water gave long needles, faintly tinged with yellow, of quercetagetin hexamethyl ether, m.p. 140.5–141.5°, lit. m.p. 141°,[6] m.p.[6,7] 142–143°.

Anal. Calcd. for $C_{21}H_{22}O_8$: C, 62.68; C, 72.68; H, 5.51. Found: 65.59; H, 5.59.

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[9] Melting points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford, England. Ultraviolet spectra were determined on a Cary recording spectrophotometer in 95% ethanol solution.

Optical Rotatory Dispersion Studies on Polysaccharides. III. Amylose, Amylopectin, and Methylcellulose[1]

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This paper is a continuation of the work in this laboratory on the conformation of polysaccharides in solution.[2,3] Solutions of amylose, amylopectin, and partially methylated cellulose were examined using the technique of optical rotatory dispersion. The method was similar to that used on protein and polypeptide solutions.[4] Typical plots of the dispersion data are shown in Fig. 1, and the values for λ_c and $[\alpha]_D$ are given in Table I for the various polysaccharide solutions.

TABLE I

ROTATORY DISPERSION CONSTANTS OF POLYSACCHARIDE SOLUTIONS

Polysaccharide	Solvent	λ_c, (mμ)	$[\alpha]_D$
Amylose (0.4 g./100 ml.)	Water	135	+200
	0.5*M* KCl	134	+201
	8*M* urea	132	+200
	1*M* NaOH	132	+162
	DMSO[a]	210	+175
Amylopectin (0.4 g./100 ml.)	Water	135	+200
	1*M* NaOH	134	+163
Methylcellulose (2 g./100 ml.)	Water	Anomalous dispersion	
solubilized at room temp.[b]	8M urea	235	−7.44

[a] DMSO = dimethylsulfoxide, see ref. 6 for details of dispersing amylose in this particular solvent. [b] See Ref. 3 for details of solubilization.

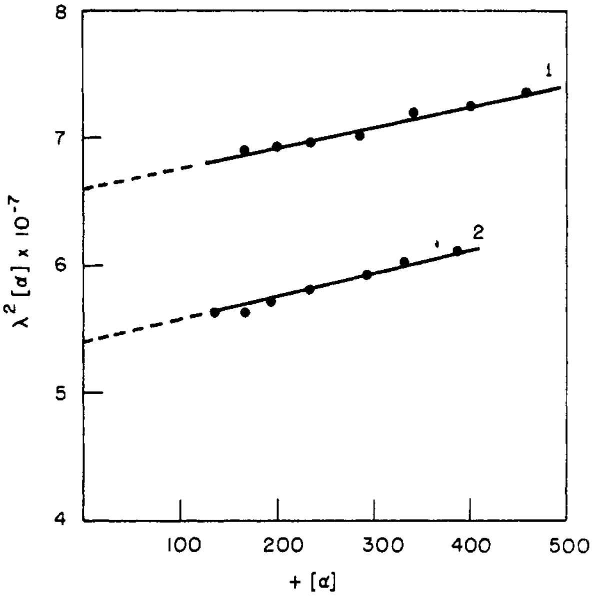

Fig. 1. Modified Drude plots of rotatory dispersion data on amylose solutions. Curve 1, amylose (0.4 g./100 ml.) in water; curve 2, amylose (0.4 g./100 ml.) in 1*M* sodium hydroxide

The value of λ_c for amylose and amylopectin in aqueous and 1*M* sodium hydroxide solutions was constant. This independence of λ_c demonstrates that rotatory dispersion is unable to measure any

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(1) Presented in part at the 138th American Chemical Society Meeting, New York, N. Y., September, 1960.

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(3) W. B. Neely, *J. Am. Chem. Soc.*, **82**, 4354 (1960).

(4) E. R. Blout, *Optical Rotatory Dispersion: Applications to Organic Chemistry*, C. Djerassi ed., McGraw-Hill, New York, 1960, chap. 17.

conformational change, such as a helix-coil transition, in these polysaccharides under the described conditions. A reasonable explanation for the decreased values of $[\alpha]$ in $1M$ sodium hydroxide therefore, might be related to a different conformation of the groups attached to the asymmetric centers of the glucopyranose units. The λ_c in this case would remain unchanged but the $[\alpha]$ of the polymer would vary. This type of interpretation lends support to the suggestion of Reeves[5] for the behavior of amylose in alkali. This author pointed out that the presence of alkali would tend to ionize the ring hydroxyls. Such an ionization would cause the axially oriented ring hydroxyls to assume equatorial positions where they would have less steric hindrance. This situation would occur in amylose if the nonreducing glucopyranose units are in one of the boat forms.

With regard to the rotatory dispersion of amylose in dimethylsulfoxide the following comments appear to be in order. A recent paper by Everett and Foster[6] demonstrated by means of intrincis viscosity and light scattering measurements that a random coil is the most probable conformation in these particular solvents. The increased value of λ_c, therefore, might be explained by either solvent interaction with the polymer or a further extension of the random coil due to the action of the highly polar dimethylsulfoxide.

No detectable differences could be noted between the dispersion curves for amylose and amylopectin. One conclusion from this observation is that the $\alpha(1 \rightarrow 6)$ branch point in amylopectin has no significant influence on the rotation of the main polymer which is a straight chain polyglucose with $\alpha(1 \rightarrow 4)$ linkages, similar to amylose.

The partially methylated cellulose when solubilized in $8M$ urea at room temperature exhibited a plain or simple dispersion curve. This is contrasted with the anomalous dispersion for methylcellulose solubilized in water under these conditions.[2,3] Previous results with this polymer indicated that the formation of aggregates was possible.[2,3] Furthermore, it was postulated that these aggregates were held together by intermolecular hydrogen bonds.

The plain or simple dispersion curve exhibited by solutions of methylcellulose in $8M$ urea further strengthens this postulation. Urea, because, of its ability to disrupt hydrogen bonds breaks up the methylcellulose aggregates. This gives rise to a solution in which all the molecules are in the random coil with the resultant simple dispersion curve.

EXPERIMENTAL

Rotatory dispersion. The present studies were conducted with a Keston photoelectric polarimeter attached to the Beckman DU Spectrophotometer. The usable range of wave lengths was from 400 to 650 mμ. The dispersion data were plotted by means of the modified Drude equation as suggested by Yang and Doty.[7]

Materials. The amylose and amylopectin were materials supplied by the Stein Hall Co.[8] In addition a commercial sample of starch was fractionated by means of *n*-amyl alcohol[9] and the amylose fraction was studied. No detectable differences between the two types of amylose could be found, consequently the comercial amylose was used in this study. The amylose and amylopectin were solubilized by dispersing an aqueous paste of the polymer in boiling water, and centrifuging the resulting solution at low speed (2000 g. for 0.5 hr.) to remove any undissolved material. The methylcellulose was similar to the material used in the previous study.[2,3]

Analytical. The specific rotations of the polysaccharide solutions were based on concentrations determined by the anthrone colorimetric procedure.[10]

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Reactivities of 17- and 20-Ketosteroids

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The reactivities of ring A and B steroid ketones towards bromination,[1a] cyanohydrin formation,[1b] and borohydride reduction[1c] have been previously reported and these measurements have recently been extended to the borohydride reduction of ring C and D ketosteroids.[2] This publication reports similar measurements on the dissociation constants of the cyanohydrins (Table I) and rates of bromination (Table II) of 17 and 20 ketones in relation to the reactivity of 3-ketosteroids.

Whereas cholestan-3-one has a low dissociation constant for its cyanohydrin comparable to that of cyclohexanone, androstanol-17-one was found to have an abnormally low dissociation constant (Table I) since its reactivity would be expected to be of the same order as cyclopentanone. Estrone has also been observed to have an exceptionally low cyanohydrin dissociation constant.[3] It is thus not surprising that the 17-keto group reacted preferentially to the Δ^4-3-keto group in androst-4-en-3,17-

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