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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TABLE I

CYANOHYDRIN DISSOCIATION CONSTANTS[a]

	$K_D \times 10^3$
Cyclopentanone[b]	56.0
Cyclohexanone[b]	6.00
Cholestan-3-one	5.40
Cholest-4-en-3-one[b]	38.4
Androstan-3β-ol-17-one	1.88
Allopregnan-3β-ol-20-one	148
Allopregn-7-en-3β-ol-20-one	109

[a] In 80% dioxane-water at 25.0°. [b] Ref. 1b.

TABLE II

RATES OF BROMINATION[a]

	$k \times 10^5$, $sec.^{-1}$
Cyclopentanone[b]	4.61
Cyclohexanone[b]	13.4
Cholestan-3-one	29.5
Androstan-3β-ol-17-one	48.0
Allopregnan-3β-ol-20-one acetate	6.08

[a] In 0.06M hydrogen chloride in 90% acetic acid at 25.0°. [b] Ref. 1a.

dione.[4] This relatively high reactivity of a 17-keto group may be due to the eclipsing effect of the hydrogen atoms[5] on C-12, or to relief of strain in the ketone group adjacent to the trans C/D ring fusion[6a] as its coordination number is increased to 4.[6b] The two allopregnan-20-one derivatives showed the expected large cyanohydrin dissociation constant, as do similarly substituted aliphatic ketones.[7] The order of reactivity found here is different from that found in borohydride reduction (3 > 17 > 20)[2], since although the reaction is analogous it is kinetically controlled by the attack of reagent on the carbonyl group. Similarly 17- and 20-ketones do not react with chloroform in the presence of potassium *t*-butoxide, whereas 3- and Δ^4-3-ketones react readily,[8] and this reaction is also irreversible.

The rate of bromination of androstanol-17-one is also larger than expected. Bromination proceeds *via* the enol and the increased ease of enolization of a 17-keto group may be again due to both the eclipsing effect and the strain in the exocyclic carbon–oxygen double bond, which should be relieved on forming the enol. The acyclic 20-keto group will not be subject to ring strain effects either reducing or favoring enolization and the allopregnan-20-one brominates at a rate intermediate between that of cyclopentanone and cyclohexanone.

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(5) A similar effect was found in the 7-keto cyanohydrin formation, Ref. 1b.

(6) (a) *cis*-8-Methyl-1-hydrindanone has the excepted high cyanohydrin dissociation constant, Ref. 3. (b)Added in press. Fishman (*J. Am. Chem. Soc.*, 82, 6143 (1960)), has recently suggested that the conformation of ring D in 16- and 17-ketosteroids is different, and a 16-ketosteroid would accordingly be expected to have a low reactivity towards addition reactions.

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EXPERIMENTAL

The rates of first order bromination and the cyanohydrin dissociation constants were determined as previously described.[1a,b]

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Identification of Quinide in Cigarette Smoke

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Palmer[1] has reported the presence of free quinic acid (1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid) in mature, fresh cigar leaves and has shown that there is a loss of quinic acid during drying of the leaves at 80°. Nagasawa[2] has developed a microcolorimetric method for the determination of quinic acid. By this method, he found quinic acid to be present in the amount of 0.23%, dry matter, in flue-cured tobacco leaves. No previous report, however, has been made of the presence of quinic acid in cigarette smoke. A depside containing quinic acid, namely chlorogenic acid (3-caffeoylquinic acid), is a major polyphenol in tobacco leaves,[3] but has not been found as yet in smoke.

Quinide (quinic acid-γ-lactone) has not been reported in tobacco leaves, nor has it previously been reported to be in cigarette smoke.

The present paper reports our identification of quinide and of quinic acid on paper chromatograms of water-soluble extracts of absolute alcohol–acetone (1:1 v/v) solutions of mainstream cigarette smoke. On paper chromatography of pure quinide in the solvent systems of Table I, some quinic acid is produced. Therefore, whether the quinic acid found on paper chromatograms of smoke solutions was actually present as such in the smoke or was produced from the quinide during paper chromatography has not been determined.

Heating dry, authentic D-(−)-quinic acid on an oil bath up to 250° produced other compounds, as revealed by paper chromatography. One of these products has been shown to be identical with a third compound found on chromatograms of

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