initial condensation, and it is probably more than a coincidence that the decrease brought about by the reaction with resorcinol is of the same order of magnitude as was found in the case of lignin and lignin sulphonic acids subjected to similar treatment.

EXPERIMENTAL. *4,6-Bis(3-methoxy-4-hydroxybenzyl)-resorcinol (III).* A mixture of vanillyl alcohol (3 g) (conveniently synthesized by the reduction of vanillin, dissolved in dilute sodium hydroxide, with a 50 % excess of sodium borohydride), resorcinol (10 g), and 2 *N* hydrochloric acid (40 ml) was refluxed for one hour. After cooling, the solution was saturated with sodium chloride, and the precipitated oil (3 g) was dissolved in ether. The ether solution was dried over anhydrous sodium sulphate, and evaporated, and the residue was triturated with ether. A large amount of oily material was dissolved and the white powder obtained (0.5 g, 13 %) was repeatedly recrystallized from benzene, yielding transparent plates, m.p. 173–174°. Found OCH_3 16.5; required for $C_{30}H_{16}O_4(OCH_3)_2$, OCH_3 16.2.

Condensation of I and II. A mixture of I or II (0.5 g), resorcinol (2 g), 50 % aqueous ethanol (20 ml), and conc. hydrochloric acid (4 ml) was refluxed for one hour. After cooling, water (75 ml) was added and the precipitate was filtered off, washed with water and chloroform and dried.

I: Found OCH_3 17.6; required for the condensation product with two molecules of resorcinol, OCH_3 17.6.

II: Found OCH_3 15.0; required for the condensation product with three molecules of resorcinol, OCH_3 15.7.

The nitrobenzene oxidations and vanillin determinations were carried out as described previously [4].

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On Quinone as Oxidising Agent in the Oppenauer-Oxidation

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In his paper on the broad applicability of the Meerwein-Ponndorf reduction of carbonyl groups by means of aluminium *iso*-propanolate Lund in 1937 [1] suggested the use of quinones for the opposite reaction: selective oxidation of >CHOH groups to >CO. The suggestion was based upon the observation that quinone was rapidly reduced to quinol by aluminium *iso*-propanolate and the quinol was immediately precipitated as aluminium quinolate. It might therefore be expected that an alcohol would react quantitatively with formation and precipitation of aluminium quinolate, as the equilibrium

$$R-CHOH-R^1 + C_6H_4O_2 \rightleftharpoons R-CO-R^1 + C_6H_4(OH)_2$$

would be displaced practically completely in favour of the right hand side, because the quinol is removed quantitatively from the solution.

In 1941 Adkins and Franklin [2], apparently without knowledge of the paper cited above, have made use of this reaction on the assumption that the high oxidation potential of quinone as compared with that of the usual aldehydes and ketones would favour the oxidation of the corresponding alcohols.

The reaction, with the use of aluminium *t*-butanolate as catalyst, was now reexamined with the purpose of finding a suitable method for the oxidation of valuable alcohols to ketones, *e.g.* in the steroid group. A few ordinary alcohols were examined first and it was found that with a reasonable excess of quinone a practically complete conversion of alcohols into ketones could be accomplished.

When the reaction was carried out in benzene solution very often a violet colour appeared during the process and in certain cases the violet compound precipitated and the reduction stopped about halfway. The intensely coloured violet compound turned out to be the aluminium "salt" of quinhydrone and was formed immediately when a benzene solution of aluminium *t.*-butanolate was added to a benzene solution of quinhydrone.

It is known that cholesterol in the Oppenauer oxidation not only is oxidised to the ketone, but simultaneously the double bond between carbon atoms 5 and 6 is moved to the 4—5 position. This is the most stable configuration because the double bond comes in conjugation to the double bond in the C = O group[3]. It was hoped that under mild oxidation conditions with quinone this rearrangement might be avoided. Experiments showed that the oxidation by means of a little more than 2 mols of quinone proceeded approximately quantitatively, but the reaction product refused to crystallise. Obviously a mixture of ketonic compounds was formed and the purpose of the investigation, thus, was not reached. Distillation of the product at low pressure (~ 0.1 mm Hg) allowed the isolation of some Δ^4-cholestenone, evidently the main product of the reaction, identified through its dinitrophenylhydrazone and its semicarbazone.

1. Oxidation of benzhydrol. 18.4 g (0.1 mol) of benzhydrol, 13 g (0.12 mol) of quinone and 19.7 g (0.08 mol) of aluminium *t.*-butanolate were dissolved in 250 ml dry benzene and refluxed with stirring on a steam-bath for 1—1.5 h. A precipitate of aluminium quinolate was removed by suction. From the filtrate benzene and *t.*-butanol was removed by distillation, finally in vacuo. The residue was dissolved in ether, the solution was purified by washing with water, dried, and the ether was removed by distillation. The residue, 17.5 g of crystals with m.p. 48°, was practically pure benzophenone. 0.468 g gave 0.910 g dinitrophenylhydrazone or 98 %. Yield of benzophenone 94 %.

If the excess of quinone was reduced to 10 % the yield dropped to 88 % and the purity of the product from 98 % to 95 %.

2. Oxidation of menthol. 8 g (0.05 mol) of menthol and 8 g (0.033 mol) of aluminium *t.*-butanolate were dissolved in benzene and 6 g (0.055 mol) of quinone were added. The solution was refluxed for 0.5 h during which the violet quinhydrone-aluminium-compound precipitated. Further 6 g of quinone were added in order to finish the oxidation, and the solution was refluxed for 15 min. The precipitate was filtered off, the solution shaken with an alcaline solution of sodium sulphite (in order to remove an excess of quinone), washed with water, dried and fractionated. Between 204° and 207° 5.6 g ~ 72 % menthone were collected, identified as dinitrophenylhydrazonem m. p. 144°.

3. *Oxidation of cholesterol.* 10 g of cholesterol (0.026 mol), 10 g of aluminium *t.*-butanolate (0.040 mol) and 6 g of quinone (0.055 mol) were dissolved in 150 ml benzene and kept at 40—45° over night. The precipitate of the quinhydrone-aluminium compound was dissolved in dilute hydrochloric acid, the benzene layer was washed with water, dried and the solvent removed by distillation. The residue was dissolved in ether and methanol added. No cholestenone was precipitated. After removal of the solvents a syrup remained from which a dinitrophenylhydrazone (m. p. 236°), a semicarbazone (m. p. 234—35°), a *p*-carboxyphenylhydrazone (m. p. 275—76°) and a phenylhydrazone (m. p. 140°) were prepared. For the dinitrophenylhydrazone of Δ^4-cholestenone m. p. 238° is reported, for the semicarbazone 234° and 237°. The two other derivatives have not been recorded in the litterature.

The syrup was distilled in high-vacuum (~ 0.1 mm Hg). The distillate crystallised and was repeatedly recrystallised from ethanol. The pure substance, faint yellow crystals with m. p. 79°, m. p. of the dinitrophenylhydrazone 236°, is evidently Δ^4-cholestenone, but the syrupy consistence of the oxydation product before distillation may indicate that other cholestenones, too, are formed during the action of quinone on cholesterol. The identical m. p. of the dinitrophenylhydrazones of the substance before and after distillation proves that the rearrangement from Δ^5- to Δ^4-cholestenone takes place during the oxidation, not during the distillation.

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On the Hexosamine Component of Seromucoid

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Glucosamine has been shown by several authors to be a constituent of serum glycoproteins. Recent investigations at this institute have shown that 2-aminogalactose, chondrosamine, occurs together with sialic acid in submaxillary mucin, in gangliosides and in the acid glycoprotein of plasma [1,2]. In the two former substances the only hexosamine obtained was chondrosamine. In the latter, chondrosamine formed the minor part of the hexosamine component, the major part consisting of glucosamine.

In order to find out if chondrosamine is present in other serum glycoproteins containing sialic acid (as indicated by the reactions characteristic of that compound)[3] the present work was undertaken. The so called seromucoid, as it is usually prepared, is certainly neither a native nor a uniform serum component, but derives probably from different serum glycoproteins. As, however, the sialic acid content fis airly high in seromucoid and this substance is comparatively easy to prepare it was chosen for the investigation.

Seromucoid was prepared mainly according to Rimington [4]. The preparation contained 5.8 per cent hexosamine and 7.9 per cent hexose. The sialic acid content was calculated to about 4 per cent. One g of this material was heated at 104° for 24 h with 5 *N* hydrochloric acid. The hydrolysate was shaken with charcoal and filtered. After evaporation in vacuo with repeated additions of methanol the filtrate was finally brought to a small volume and dry methanol was added. After standing overnight in an exsiccator a crystalline deposit had formed and was collected. The crystals were shown by the X-ray powder diagram to be α-glucosamine hydrochloride. When more methanol was added glucosamine crystals continued to form for a couple of days. The mother liquor was then brought to a thick syrup and dry methanol was added again. After three weeks in the exsiccator a crystalline mass could be collected. The X-ray powder diagram of these crystals were completely identical to that of an authentic specimen of β-chondrosamine hydrochloride (Fig. 1). In total about. 5 mg of the chondrosamine salt were isolated.

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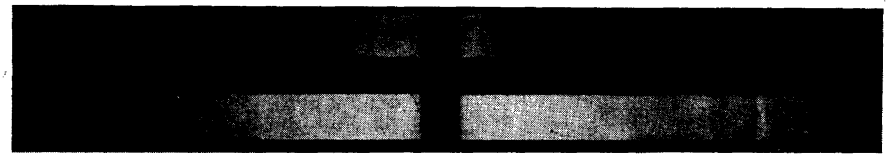

Fig. 1. I. Powder diagram of β-chondrosamine hydrochloride. II. Powder diagram of last aminosugar fraction obtained from seromucoid hydrolysate.