TABLE I

Copolymerization of acrylonotrile and vinylpyrrolidone at 56° C initiated by AIBN

AN mole% feed	AN in copolymer	f obs.	f calcd.	F^2/f	$(F - F)/f$
0·2852	0·5398	1·170	1·360	0·137	0·0584
0·4076	0·7535	3·018	2·303	0·156	0·4603
0·5171	0·7852	3·650	3·650	0·313	0·7770
0·6162	0·8404	5·268	5·268	0·489	1·3012
0·7060	0·8838	7·598	7·598	0·763	2·0920
0·7893	0·9240	11·947	11·847	1·174	3·4300

The dyeing was carried out at 75° C for 1 hour. The residual dye solution was estimated by visible spectrum using *uv* vis specord. The percentage of the dye uptake is given in Table II. The dyeability was increased with respect to both the acid and the basic dyes.

TABLE II

Dye uptake by polyacrylonitrile and poly(acrylonitrile-Co-vinylpyrrolidone)

Sample	Rhodamine T dye uptake %	Acid orange II Dye uptake %
PAN film ..	16·40	15·00
Copolymer film	20·50	28·50

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NUCLEAR REDUCTION IN FLAVONOIDS

IN the biogenetic theories to account for the formation and interconversion of flavonoid compounds in nature, nuclear oxidation (introduction of phenolic hydroxyl groups) and nuclear reduction (removal of phenolic hydroxyl groups) have been definitely shown to occupy an important place[1,2]. Nuclear oxidation of phenolic compounds both with alkaline persulphate and with alkaline hydrogen peroxide (through an *ortho*-hydroxy-aldehyde system) has been taken as a laboratory model for the biogenetic introduction of phenolic hydroxyl group in these compounds and the typical conversion of 3, 7, 3′, 4′-O-tetramethylquercetin into 3, 7, 3′, 4′-O-tetramethylgossypetin[3] has been invoked as a valid proof for the hypothesis that the former is a natural precursor for the latter. However, the reversal of this process (removal of phenolic hydroxyl group), *viz.*, nuclear reduction, has remained for a long time only as a hypothesis without laboratory parallel until a number of such nuclear reductions were accomplished in the laboratory[4–7] and the method involves the preparation of the phenolic tosylates and their subsequent hydrogenolysis using Raney nickel.

In the present communication, we wish to report the successful conversion of a gossypetin derivative into a quercetin derivative by the process of nuclear reduction. This would eventually close the hitherto unfilled gap in the biogenetic hypothesis of the formation of quercetin from gossypetin with an experimental support.

The necessary starting material for this purpose is a suitable gossypetin derivative in which the 8-hydroxyl group is free. Since gossypin (the 8-glucoside of 3, 5, 7, 8, 3′, 4′-hexahydroxyflavone) is known to occur in the flower petals of *Hibiscus vitifolius*[8],

it was decided to procure the starting material from this source. However, extraction of fresh flower petals of this plant yielded a mixtue of gossypin[8] and the 8-O-glucuronide of gossypetin[9] which could be separated on a cellulose column. The structure of the two pigments could be confirmed individually by the technique of methylation and hydrolysis whence the former gave 3, 5, 7, 3', 4'-O-pentamethylgossypetin and glucose while the latter afforded the same flavone derivative and glucuronic acid. Enzymatic hydrolysis, using the enzymes (β-glucosidase as well as β-glucuronidase), and also U.V. spectral data with and without the addition of the various shift reagents confirmed these conclusions. Since in the above two glycosides, only the 8-hydroxyl group is blocked, the mixture of the two compounds could directly be used for our studies without any need to separate the constituents.

A suspension of the dry and finely powdered glycosidic mixture (1 g), isolated from the fresh flower petals of *H. vitifolius*, in dry acetone (200 ml) was methylated with freshly distilled dimethyl sulphate (8 ml) and ignited potassium carbonate (20 g) by refluxing the mixture for 50 h (negative ferric reaction). The methylation product (1 g) could not be satisfactorily crystallized and was directly hydrolyzed by refluxing with aq. H_2SO_4 (7%; 50 ml) for 2 hr. The hydrolyzate, on cooling in ice, slowly deposited 8-hydroxy-3, 5, 7, 3', 4'-pentamethoxyflavone (700 mg), m.p. 196–198° (lit.[10] m.p. 196–198°); acetate (Ac_2O and pyridine), m.p. 215–216° (lit.[10] m.p. 215–216°).

Tosylation of the above partial methyl ether of gossypetin using the hydroxy compound (500 mg), crystallized toluene *p*-sulphonyl chloride (400 mg) and ignited potassium carbonate (5 g) in dry acetone (150 ml) medium gave 3, 5, 7, 3' 4'-pentamethoxy-8-tosyloxyflavone as colourless plates (from alcohol) (200 mg), m.p. 144-146° (Found : C, 59·6; H, 4·7; $C_{27}H_{26}O_{10}S$ requires C, 59·8; H, 4·8%).

The above tosyl ester was subjected to nuclear reduction as follows : To a clear solution of the tosyl ester (200 mg) in ethanol (500 ml), Raney nickel catalyst (2 g) was added and purified H_2 gas was bubbled through the suspension of the above, with stirring, for 5 hr. After filtration, the residue was washed repeatedly with ethanol and the combined ethanolic solution evaporated. The residue, obtained after removal of the alcohol, was taken in benzene and the benzene solution was washed with 1% aq. NaOH solution and then with water. The organic layer was dried (anhyd. Na_2SO_4) and evaporated when a residue was obtained which was separated by T.L.C. over silica gel plates using toluene-ethyl acetate-formic acid (5:4:1) as the irrigating solvent. The slow-moving band, on elution with methanol, yielded crystalline pentamethylquercetin[11] (3, 5, 7, 3', 4'-pentamethoxyflavone) (50 mg), m.p. and mixed m.p. 151-152°. Thus starting from a derivative of gossypetin, a quercetin derivative could be prepared in the laboratory.

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DIPOLE MOMENT AND INTRAMOLECULAR HYDROGEN BONDING IN ORTHO-SUBSTITUTED PHENOLS

We wish to report here certain interesting features of the dipole moments of some ortho-substituted phenols and anisoles and the corresponding para-substituted compounds and also an explanation for them. It may be seen from Table I that the difference between the dipole moments ($\Delta\mu$) of an ortho-substituted anisole and the corresponding ortho-substituted phenol is large compared to a similar difference for the corresponding para derivatives.

The ortho-halogenophenols and ortho-nitrophenol exist to a larger extent in the *s-cis* configuration (I) due to the stabilization by intramolecular hydrogen bonding; this leads to a lower dipole moment in these compounds. [*cf.* Table I. The calculated dipole moment of a *cis*-form is smaller than the *s*-trans form (II) in these compounds[1]]. On the other hand in the ortho-substituted anisoles the introdction of a substituent Y into the ortho-position of the benzene nucleus leads to considerable steric hindrance for the *s-cis* orientation which becomes energetically less favourable and the *s*-trans orientation predominates in almost all the ortho-substituted anisoles. The large contri