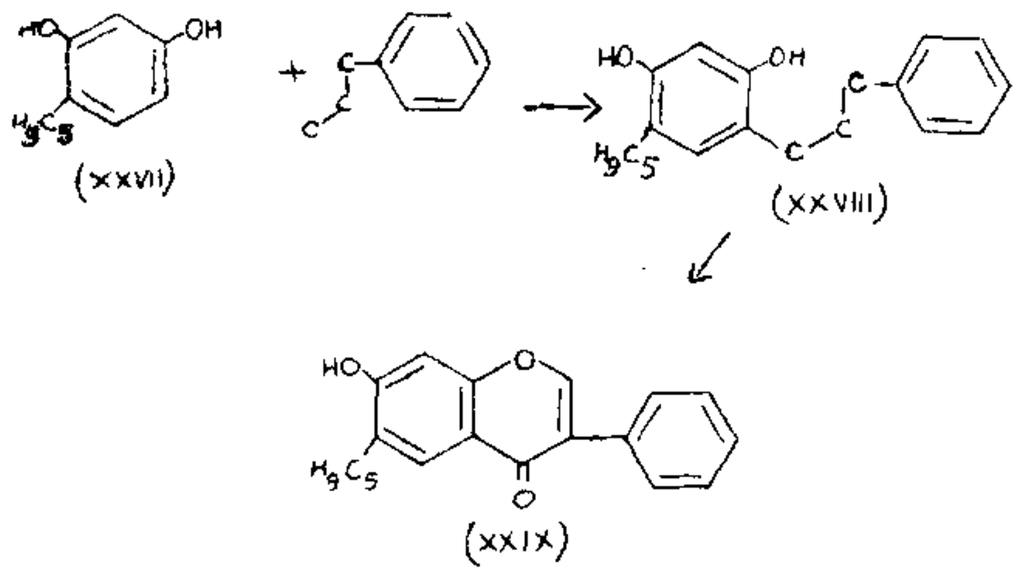
the linear compounds would involve entry of this unit in the position corresponding to 6. This would be possible if in these cases a C_5 unit got attached to the original C_6 component of the flavonoid before it was linked with the C_9 component.



1. Nag, N. C., Banerjee, H. N. and Pain, A. K., *Trans. Bose Research Inst.*, 1935–36, **11**, 83.
2. Norton, L. B. and Hansberry, R., *J. Amer. Chem. Soc.*, 1945, **67**, 1609.
3. Simonitsch, E., Frei, H. and Schmid, H., *Monatsh.*, 1957, **88**, 541; Rajagopalan, P. and Kosak, T. I., *Tetrahedron Letters*, 1959, **21**, 5.
4. Eisenbeiss, J. and Schmid, H., *Helv. Chim. Acta*, 1959, **42**, 61.
   Chatterjea, J. N. and Prasad, N., *Ber.*, 1964, **97**, 1252.
5. Bickel, H. and Schmid, H., *Helv. Chim. Acta*, 1953, **36**, 664.
6. Crombie, L. and Whiting, D. A., *J. Chem. Soc.*, 1963, p. 1569.
7. Chibber, S. S. and Seshadri, T. R., *Curr. Sci.*, 1965, **34**, 238.
8. Barz, W., Patschke, L. and Grisebach, I., *Chem. Comm.*, 1965, p. 400.
9. Aneja, R., Mukerjee, S. K. and Seshadri, T. R., *Tetrahedron*, 1958, **4**, 256.
10. Harper, S. H., *J. Chem. Soc.*, 1939, p. 812; 1940, pp. 309 and 1178.
11. Barton, D. H. R., Kirby, G. W., Taylor, J. B. and Thomas, G. M., *Ibid.*, 1963, p. 4545.
12. Ollis, W. D., *Abstracts of International Symposium on Natural Products, Japan*, 1964, p. 391 and private communication.
13. Johnson, A. P., Pelter, A. and Barber, M., *Tetrahedron Letters*, 1964, p. 1267.
    Pelter, A. and Stainton, P., *Ibid.*, 1964, p. 1209.
    — and Johnson, A. P., *Ibid.*, 1964, p. 2817.
14. Aghoramurti, K., Kukla, A. S. and Seshadri, T. R., *Curr. Sci.* 1961, **30**, 218; Kalra, V. K., Kukla, A. S. and Seshadri, T. R., Unpublished work.

ANALYSIS OF PHENOL, HYDROQUINONE, QUINONE AND MALEIC ANHYDRIDE IN A MIXTURE

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THE study of catalytic vapour phase oxidation of benzene involves the problem of estimating phenol, hydroquinone, quinone and maleic anhydride in a mixture of all these along with unreacted benzene. Though there are a number of methods for the estimation of the individual compounds, there has been no report of any detailed work pertaining to the interferences by the other compounds present while estimating each of these in a mixture. Denton *et al.*[1] as well as Marisic[2] in their studies on the oxidation of aromatic compounds have employed a procedure involving separation of the compounds and subsequent analysis of them individually. However, it is preferable to estimate each constituent in a mixture as such than employ a quantitative separation followed by individual estimation. With this in view, synthetic mixtures containing known amounts of phenol, hydroquinone, quinone and maleic anhydride were prepared and a procedure for estimating the compounds was evolved after extensive testing.

A large number of methods of estimating phenol are based on the bromination of phenol followed by determination of the excess reagent. Phenol being acidic can also be determined by alkalimetric titration. However, in presence of carboxylic acids such estimations are not possible. Also the highly sensitive colorimetric method cannot be employed here since the presence of even small amounts of quinone and hydroquinone will modify the characteristic phenol colouration considerably.[3] Hence bromination method was adopted here for the estimation of phenol in these synthetic mixtures. The bromination was carried out using bromate-bromide reagent.[4]

Reagents :

(*i*) 0·1 N sodium thiosulphate solution prepared by dissolving 24·8 g. of $Na_2S_2O_3.5H_2O$ in one litre of water.

(*ii*) Brominating solution consisting of 3·5 g. of potassium bromate and 55 g. of potassium bromide in one litre of solution.

(iii) Concentrated hydrochloric acid (sp. gr. 1.2).
(iv) 20% potassium iodide solution.
(v) 1% starch solution.

Some of the results of such determinations are indicated in Table I.

TABLE I

Results of phenol estimation in synthetic mixture

Amount in grams taken				Phenol determined	
Phenol	Hydro-quinone	Maleic anhydride	Quinone	Without correction	With correction
0·7528	..	0·1028	..	0·7968	..
0·7968	..	0·1028	..	0·8041	..
0·7528	..	..	0·0146	0·7528	..
0·7528	0·07685	..	..	1·0349	0·7598
0·7528	0·07685	..	..	1·0330	0·7579
0·01356	0·01618	0·01082	0·003892	0·01685	0·0145
0·3945	0·0721	0·02204	..	0·4446	0·3922

It is seen from Table I that the bromometric method of estimating phenol is quite satisfactory even in the presence of maleic anhydride. Bromination is also a method of estimating the unsaturation in maleic anhydride.[5] In spite of this, maleic anhydride is found to have no significant effect on phenol estimation, probably due to the differences in the conditions employed for bromination in the two cases. For the bromination of maleic anhydride, a catalyst like mercuric sulphate as well as longer period of reaction is necessary. In one of the estimations in presence of maleic anhydride a high deviation of 5·52% (estimated value of 0·7968 g for 0·7528 g) was obtained because of carrying out the bromination for more than half-an-hour instead of the fifteen minutes normally employed. Otherwise, when normal procedure is employed phenol estimation can be carried out in presence of maleic anhydride within one per cent deviation. The table also indicates that quinone does not interfere in the estimation. The results further indicate that the presence of hydroquinone very much affects the phenol estimation. This is contrary to the observation of Kolthoff *et al.*[6] who indicate that in the bromometric determination of phenols, compounds with two hydroxyl groups in the ortho or para position do not react with bromine at room temperature. Experimentally it has been found that the volume of brominating solution consumed while brominating a sample of the synthetic mixture is in excess of that required for bromination of phenol alone in the mixture. This excess volume is found to correspond to computed volume assuming the following reaction between bromine and hydroquinone.

$$C_6H_4(OH)_2 + Br_2 \longrightarrow C_6H_4O_2 + 2HBr.$$

Thus, on computing estimated value of phenol after taking into account the correction for bromine consumption due to hydroquinone, satisfactory values are obtained as shown in Table I. Hence this method can be employed for the estimation of phenol in a mixture of phenol, hydroquinone, quinone and maleic anhydride provided an independent estimation of hydroquinone and thus the bromine consumption due to hydroquinone can be obtained. Hydroquinone can be estimated by quantitatively oxidising it to quinone and determining the excess of reagent. The oxidation can be brought about by iodine,[7] dichromate[8] or ceric sulphate.[9] It was found that iodometric estimation of hydroquinone could be carried out within 2% deviation in presence of phenol, maleic anhydride and quinone.

For the estimation of quinone, use was made of its reaction with an acidified solution of potassium iodide[10] and was found satisfactory.

Alkalimetric titration was found fairly accurate in estimating maleic anhydride in the synthetic mixture, though there have been reports of difficulty in estimating anhydride in presence of quinone.[11] The results which are accurate to within 2% are further improved if the solution of the mixture is boiled before carrying out the analysis for anhydride. Similar observations have been made by Bhattacharya and Venkataraman.[12]

1. Denton, V. I., Doherty, H. G. and Krieble, R. H., *Ind. Eng. Chem.* 1950, **42**, 777.
2. Marisic, M. M., *J. Am. Chem. Soc.*, 1940, **62**, 2312.
3. Ju Chin Chu. Ai, H. C. and Othmer, D. E., *Ind. Eng. Chem.*, 1953, **45**, 1267.
4. Day, A. R. and Taggart, W. T., *Ibid.*, 1928, **20**, 545.
5. Lucas, H. J. and Pressman, D., *Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 140.
6. Kolthoff, I. M. and Belcher, R., *Volumetric Analysis*, 1957, **3**, 536 (Interscience).
7. — and Lee, T. S., *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 452.
8. Bhaskara Rao, K., *Z. anal. Chem.*, 1963, **185** (4), 286.
9. Furman, N. H. and Wallace, J. H., *J. Am. Chem. Soc.*, 1930, **52**, 1443.
10. Richter Victor Von, *The Chemistry of Carbon Compounds* (Elsevier), 1946, **3**, 186.
11. Shreve, R. N. and Welbron, R. W., *Ind. Eng. Chem.*, 1943, **35**, 279.
12. Bhattacharya, S. K. and Venkataraman, N., *J. Appl. Chem.*, 1958, **8**, 728.