NUCLEAR OXIDATION OF EUXANTHONE

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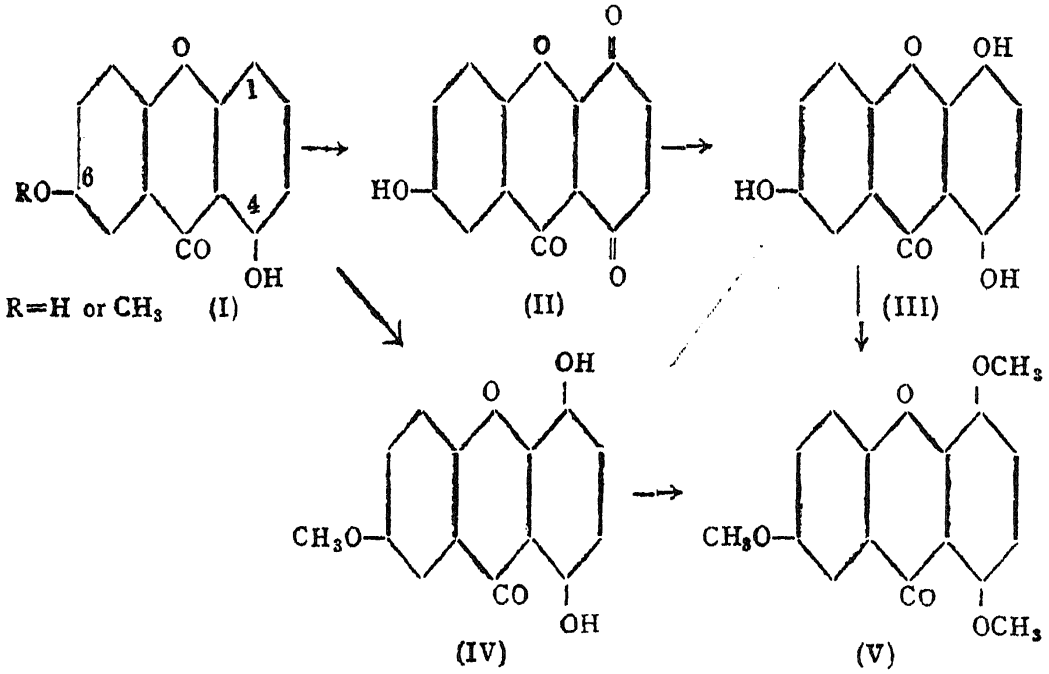
Along with quercetin and chrysin, Nierenstein carried out the nuclear oxidation of euxanthone[1] (I, R = H) also using chromic acid in acetic acid solution. The immediate product was a quinone which could be reduced to a quinol and they were given the constitutions (II and III). Since in the other two cases[2] his results have been found to be wrong, verification of this example also has now been taken up. For this purpose the method of oxidation with persulphate which has been proved to be quite reliable in a large number of cases of hydroxy-flavones[2] is adopted.



Experiments employing euxanthone itself for the oxidation have not been successful; another reaction seems to be taking place predominantly and the yield of the required oxidation product is found to be extremely poor. However the monomethyl ether of euxanthone[3] (I, R = CH_3) could be oxidised readily to a compound having all the properties of a quinol and hence it should be given the constitution (IV). On methylation it yields the trimethyl ether (V) and on demethylation the trihydroxy compound (III) which is now named 1-hydroxy-euxanthone. During the demethylation with hydriodic acid there is a possibility of isomerisation to 3: 4: 6-trihydroxy-xanthone, as found in the case of 5: 8 and 5: 7: 8-methoxy-flavones.[4] But no such change appears to take place here since on

remethylating the trihydroxy-compound the trimethyl ether is found to be identical with the product of direct methylation of (IV).

The properties of the compounds obtained in the course of the present work are summed up in the following table and are compared with those recorded by Nierenstein. They do not agree and hence his claim is again not supported. 1-Hydroxy-euxanthone differs markedly from its isomer, gentisein particularly with regard to the colour of the substance and its reactions with sodium hydroxide and *p*-benzoquinone.

	Nierenstein's data	Present data
Trihydroxy- xanthone ..	Pale yellow needles, M.P. 328–30°	Orange yellow rectangular prisms, M.P. 300–02°
Triacetyl-derivative ..	M.P. 226–30°	188–90°
Trimethyl-ether ..	M.P. 194–95°	158–60°

Experimental

Monomethyl-euxanthone[3].—This is more conveniently prepared in the following manner.

A solution of euxanthone (1·5 g.) in anhydrous acetone (50 c.c.) was treated with dimethyl sulphate (0·7 c.c.) and freshly ignited potassium carbonate (5 g.). After refluxing for 6 hours the solvent was distilled off, the residue treated with water and the yellowish brown solid which was formed was filtered, washed with water and purified by crystallisation from alcohol. It came out in the form of glistening pale yellow plates melting at 129–30°. Yield 1 g.

6-*Methoxy*-1 : 4-*dihydroxy-xanthone* (*IV*).—

The above monomethyl-euxanthone (1 g.) was dissolved in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (1·8 g. in 25 c.c.) and the clear yellow solution was stirred and treated dropwise with a solution of potassium persulphate (2 g. in 75 c.c.) during the course of two hours. The deep greenish brown solution was allowed to stand for 24 hours and just acidified when the unchanged methyl ether was precipitated. It was filtered off, washed and the filtrate extracted twice with ether. The clear brown aqueous solution was treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (25 c.c.) and heated in a boiling water-bath for 30 minutes. The glistening yellow crystalline solid that separated out was filtered after cooling and washed with water. Some more of the product could be obtained from the filtrate by extracting with ether. Yield 0·4 g. It crystallised from ethyl acetate in the form of golden yellow long rectangular

plates melting at 280–82° with decomposition. (Found: C, 64·7; H, 3·4; $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·7%.) It was sparingly soluble in alcohol, ethyl acetate and acetone. The alcoholic solution gave a deep brown colour with ferric chloride and brown-red with *p*-benzoquinone. It readily dissolved in aqueous sodium hydroxide (5%) to a deep reddish violet coloured solution.

1 : 4 : 6-*Trimethoxy-xanthone* (*V*).—

The above dihydroxy compound (0·1 g.) was dissolved in anhydrous acetone (20 c.c.) and the solution treated with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (3 g.). After refluxing for 6 hours the solvent was distilled off. Water was added to the residue and the colourless solid left behind was filtered, washed and crystallised successively from a mixture of benzene and petroleum ether and from alcohol. It came out in the form of colourless narrow rectangular plates and flat needles melting at 158–60°. (Found: C, 67·5; H, 4·7; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). It was sparingly soluble in ether and easily in alcohol and benzene. It was insoluble in aqueous sodium hydroxide and did not give any colour with alcoholic ferric chloride. In concentrated sulphuric acid it dissolved producing a deep red colour.

1 : 4 : 6-*Trihydroxy-xanthone* (*III*).—

The dihydroxy compound (IV) (0·2 g.) was dissolved in acetic anhydride (3 c.c.) and treated with hydriodic acid (6 c.c.) slowly with cooling. The deep reddish brown solution was gently refluxed for 1 hour, cooled, diluted with water and the free iodine present was removed by the addition of sufficient sodium sulphite. The orange coloured product was filtered, washed well with water and purified by crystallising from a mixture of ethyl acetate and benzene. It separated out in the form of orange yellow aggregates of short rectangular prisms melting at 300–02°. (Found: C, 63·6; H, 3·3; $C_{13}H_8O_5$ requires C, 63·9; H, 3·3%.) It was readily soluble in alcohol, acetone and ethyl-acetate and sparingly in ether. In alcoholic solution it gave a brown colour with ferric chloride and brown-red with *p*-benzoquinone. In 5% aqueous sodium hydroxide the solution had a deep blood-red colour. It dissolved in concentrated sulphuric acid giving a red solution.

The above trihydroxy compound (0·1 g.) was acetylated using acetic anhydride (3 c.c.) and a drop of pyridine. The acetate crystallised from alcohol in the form of colourless needles melting at 188–90°.

The trihydroxy compound (0·1 g.) was methylated in anhydrous acetone solution (20 c.c.) with dimethyl sulphate (0·5 c.c.) and potassium carbonate

(5 g.). The methyl ether crystallised from alcohol in the form of colourless narrow rectangular plates melting at 158–60 alone or in admixture with the methylation product of 6-methoxy-1 : 4-dihydroxy-xanthone.

SUMMARY

The 6-methyl ether of euxanthone has been oxidised to 6-methoxy-1 : 4-dihydroxy-xanthone by means of alkaline persulphate. By demethylation with hydriodic acid 1 : 4 : 6-trihydroxy-xanthone has been obtained. This compound and its derivatives differ from those obtained by Nierenstein by the oxidation of euxanthone itself with chromic acid and subsequent reduction.

REFERENCES

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