OCCURRENCE OF 3, 4, 2′, 4′, 6′-PENTAHYDROXY CHALKONE IN THE PETALS OF *HELICHRYSUM BRACTEATUM*

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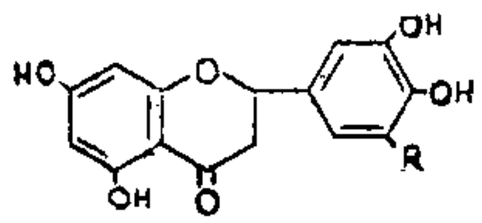
EARLIER Narasimhachari and Seshadri[1] made a study of the natural occurrence of hydroxy chalkones and flavanones and also the stability of natural and synthetic compounds in the presence of acids and alkali and came to the conclusion that chalkones having 2′, 6′-hydroxy substituents are unstable and therefore do not occur free because they are readily converted into the corresponding flavanones. The examples were naringenin, eriodictyol, hesperitin and their glycosides which commonly occur in plant materials; but the corresponding chalkones are not found. In special cases where the glycosides of the chalkones occur free, the sugar groups are found linked to one of the 2′ and 6′-hydroxyl groups: *e.g.*, neo-sakuranin[2] and isosalipurposide.[3] Based on these considerations the constitutions of carthamin and xanthohumol[4] were suggested to be 6′-glucoside and 6′-methyl ether respectively of the corresponding chalkones. Later on from other data these have been proved to be correct.[5,6]

However, Shimokoriyama[7] recorded that in the case of naturally occurring 7-glycosides of flavanones, the corresponding chalkone glycosides can be made in the laboratory under carefully controlled conditions. The chalkone glycosides can be kept in the cold, particularly in the absence of acids and some of them can be even crystallised. They were unstable in the presence of acids and rapidly underwent change into flavanones.

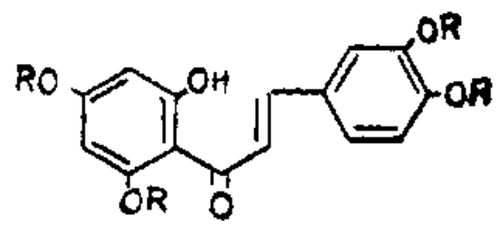
More recently certain naturally occurring compounds[8] have been given the unstable dihydroxy-chalkone structure. It seems to us that correct information about these chalkones have not so far been obtained because they are not occurring free so commonly and the conditions of synthesis are too unsuitable for their satisfactory preparation: *e.g.*, Farkas, Nogradi and Major[9] have recently synthesised 4, 2′, 4′, 6′-tetrahydroxy chalkone 4′-β-*d*-glucoside and observed that it is highly unstable to heat. The melting point could not be determined because of the rapid isomerisation and further the sample could not be dried to remove water of crystallisation.

Our recent study of flowers of *Helichrysum bracteatum* seems to indicate that the above type of unstable chalkones are more commonly occurring than we originally imagined. A few years back Rimpler, Langhammer and Frenzel[10] studied these flowers and noted that besides other components they contain the flavanones eriodictyol (I) and 5′-hydroxy eriodictyol (II). These were accompanied by the related chalkone glycosides which on hydrolysis with acids gave rise to these flavanones and were therefore reported to be the chalkone 6′-glycosides. We have now examined the ether extract of these flowers which is free from glycosides.

In our present investigation the flowers were collected from the University garden. The air-dried petals were first extracted with light petroleum (60–80°) and then with ether. Ether extract was evaporated and the residue subjected to chromatographic examination when it has been found to contain four compounds two of which having higher R_f values were almost colourless but developed an yellow colouration when exposed to ammonia and were in negligible amounts. Separation on a preparative scale was effected using the descending paper chromatography technique and the bands were cut and eluted with methanol. For the chromatography the upper phase of butanol, acetic acid, water system (4 : 1 : 5, v/v) was more convenient in comparison to other solvent systems.



I, R = H
II, R = OH



III, R = H
IV, R = CH_3

The compound with R_f 0·65 BAW[b] has been studied in greater detail. It has been obtained as an yellow crystalline solid. It gave a greenish-brown colour with alcoholic ferric chloride and an orange red colour with ammonia. Mg/HCl and Zn/HCl reactions were negative. It gave a positive borohydride colour reaction (magenta). The colour reactions and U.V. characteristics showed that it is a chalkone. $\lambda_{max}^{methanol}$ 282, 327 (infl.), 376 (the band at 376 mμ being more intense); with $AlCl_3$, 282, 475-480; with NaOAc, 325, 403; with NaOMe, 325, 430–435 and with boric acid and NaOAc, 280, 320, 410 mμ. The

chalkone did not contain any methoxyl group (micro ziesel). It was found to be identical with the one obtained from eriodictyol (co-chromatography) proving it to be 3, 4, 2', 4', 6'-pentahydroxy chalkone (III).

According to Narasimhachari and Seshadri eriodictyol when treated with 10% aqueous potash and kept at room temperature for ½ hr. and acidified in the cold was recovered unchanged. We have used 20% aqueous alkali and 12 hrs.; on chromatography the product showed one weak yellow spot and another one which developed yellow colour (major portion) on exposure to ammonia. When Shimokoriyama's method,[7] boiling with aqueous potash (0·5 g. in 1 ml. of water) for 2 mts. is adopted the crude product showed a single yellow spot and a very faint spot due to some eriodictyol. The chalkone had a melting point of 140–42°; usually the melting point of a chalkone is about 10° lower than the corresponding flavanone; eriodictyol melts at about 267°. The lower melting point of the chalkone may be due to rapid isomerisation. It is highly unstable in presence of acids and also to heat and yields eriodictyol when boiled with alcoholic hydrochloric acid.

On methylation with dimethyl sulphate and potassium carbonate in acetone (10 hr.) it gave a tetramethyl ether, m.p. 146–47°, which gave a positive ferric reaction, and has been found to be identical with synthetic 2'-hydroxy-3, 4, 4', 6'-tetramethoxy chalkone (IV). The identity was proved by T.L.C. and mixed melting point. The n.m.r. spectrum of the methyl ether was taken in $CDCl_3$ using tetramethyl silane as the internal standard and the signals are given below: −4·45 τ (2'-Hydroxy proton); 2·28 τ (olefinic protons); 3·2 to 2·7 τ (3 aromatic protons of A ring at 2, 5 and 6); 4·03 and 3·87 τ (two meta coupled protons at 3' and 5'; J = 3 CpS) and 6·17 and 6·09 τ (12 protons of the methoxyls at 3, 4, 4', 6').

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EFFECT OF CHLORINATION OF WATER ON CONTROL OF BACTERIAL LEAF BLIGHT OF RICE, CAUSED BY *XANTHOMONAS ORYZAE* (UYEDA AND ISHIYAMA) DOWSON

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RECENTLY, Thompson[1] reported that spread of bacterial stalk rot of corn could be checked by chlorination of water in sprinkler irrigation to give a concentration of 1 ppm residual chlorine. Our attention was drawn to these results by Dr. B. L. Renfro of the Rockefeller Foundation, New Delhi, with the suggestion that this method could be given a trial for the control of bacterial blight of rice. Since infection of *Xanthomonas oryzæ* spreads rapidly through irrigation water (Inoue *et al.*,[2] Tagami *et al.*[3]) it was thought worthwhile to conduct a field trial to study the effect of chlorination of water on control of bacterial blight. The results of the field trial conducted at the Central Rice Research Institute Farm, Cuttack, during Kharif, 1966 are discussed below:

The chlorine application was tried on large plots of the varieties *Taichung Native*-1 and *IR*-48 (*Taichung Native*-1 × *Taichung*-65), the high-yielding varieties which are very susceptible to bacterial blight. There were 3 plots of 50 cents of each of the two varieties covering a total area of 3 acres.

The treatments included were: (*i*) Application of chlorine at 1 ppm in the form of bleaching powder containing 30% chlorine (2 kg./ha.), (*ii*) Application of 5 sprayings with antibiotic (Streptocycline) + copper oxychloride (3 gm. antibiotic + 113 gm. of copper oxychloride in