glycol system. $\delta$ 2·0 (s)-3H, 2·08 (s)-3H for two -COCH$_3$; $\delta$ 3·63 (s)-3H for -COOCH$_3$; $\delta$ 4·85 (d)-1H (J = 10 Hz) for C$_2$-$\alpha$H; $\delta$ 5·15 (m)-1H for C$_2$-$\beta$H; $\delta$ 5·31 (t)-1H for C$_{12}$-H. All these spectral measurements suggest that the dihydroxy triterpene mono carboxylic acid could be maslinic acid, 2$\alpha$, 3$\beta$-dihydroxy olen-12-en, 28-oic acid. The identification was finally confirmed by comparison with an authentic sample, earlier isolated in these laboratories from *Eugenia jambolona*[6]. It was first reported in *Crataegus oxyacantha*[8] and also from several plants of Myrtacece[9,10].

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## A NEW SYNTHETIC BIFLAVONE

BIFLAVONES are usually synthesised by the simple or crossed Ullmann condensation of the appropriate iodoflavones [1,2], the dehydrogenation of the bichalcones[3], double Baker-Venkataraman transformation of the suitable biphenyl derivatives[4,5] followed by ring closure and the Allan-Robinson condensation of the biphenyl derivatives[6].

The Algar-Flynn-Oyamada (AFO)[7,8] oxidation of chalcones gives flavonols through the intermedicy of flavononols. In the present communication, we wish to report the synthesis of the biflavone (3) by the oxidation of the bichalcone (2).

Reaction of 2, 2'-dihydroxy-4, 4',6,6'-tetramethoxy-3,3'-diacetylbiphenyl[4,5] (1) with anisaldehyde in presence of alkali produced the bichalcone[5] (2).

Reaction of alkaline hydrogen peroxide on the bichalcone (2) in pyridine at 65° gave I-3, II-3-dihydroxy-I-4', II-4', I-5, II-5, I-7, II-7-hexamethoxy [I-8, II-8] biflavone (3); m.p. 228-229°. IR-spectrum of the biflavone (3) showed absorption at 1630 (chelated carbonyl) and 3300 cm$^{-1}$ (OH). Mass spectrum showed molecular ion peak at m/e 654 and the general fragmentation pattern was typical of a C-C-linked biflavone. (3) on acetyl tion with acetic anhydride and pyridine gave the diacetate (4), m.p. 175-176°. IR-spectrum of compound (4) showed absorption at 1640 (C=O) and 1780 cm$^{-1}$ (acetate). Acetylation of the 3-hydroxyl produced the shift (+ 10 cm$^{-1}$) to higher wavelength. NMR spectrum of the diacetate (60 MHz, CDCl$_3$, TMS as internal standard, $\delta$ ppm); 1·95 (s, 2 OAc), 3·7 (s, 2 OMe), 3·80 (s, 2 OMe), 4·1 (s, 2 OMe), 6·5 (s, 2 H), 6·6 (d, J = 10 Hz, 4 H) and 7·2 (d, J = 10 Hz, 4 H). The doublets at 6·6 and 7·2 integrating to a total of 8 protons and forming a clear A$_2$B$_2$ pattern, are due to protons at I-3', II-3', I-5', II-5' and I-2', II-2', I-6', II-6' positions. This typical A$_2$B$_2$ pattern is usually observed when C-4' is substituted. A comparison of the NMR spectrum of the diacetate (4) with those of the methyl ethers of biflavones[1,9-11] indicates that the singlet at 6·5 is due to the two equivalent protons at the I-6 and II-6 positions.
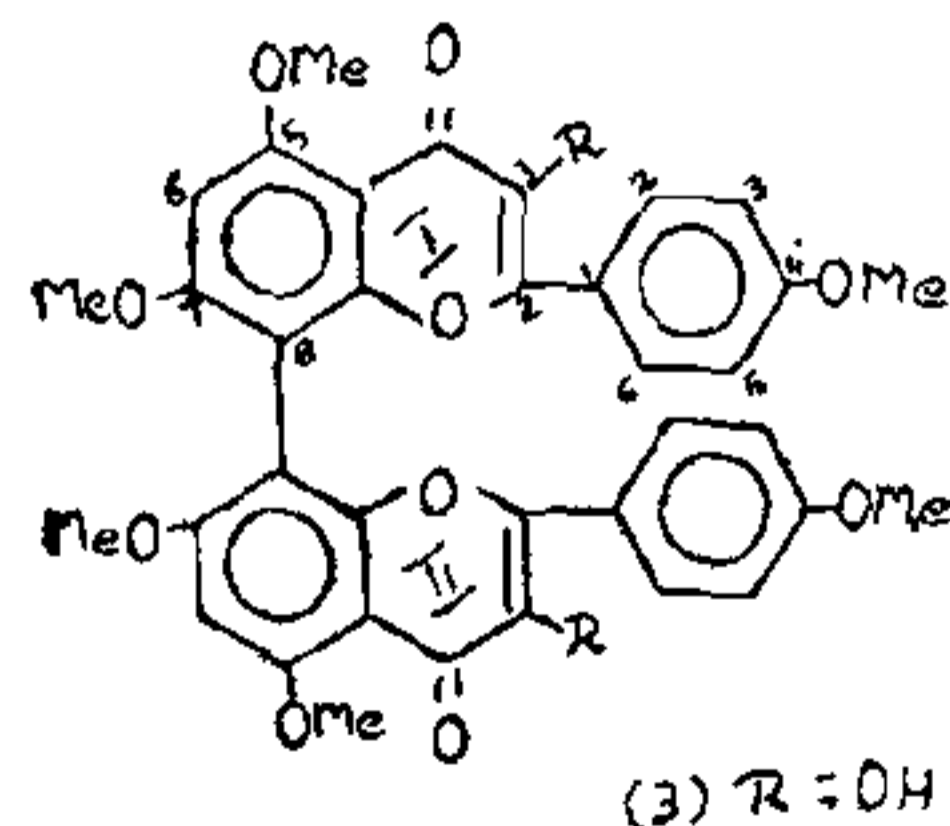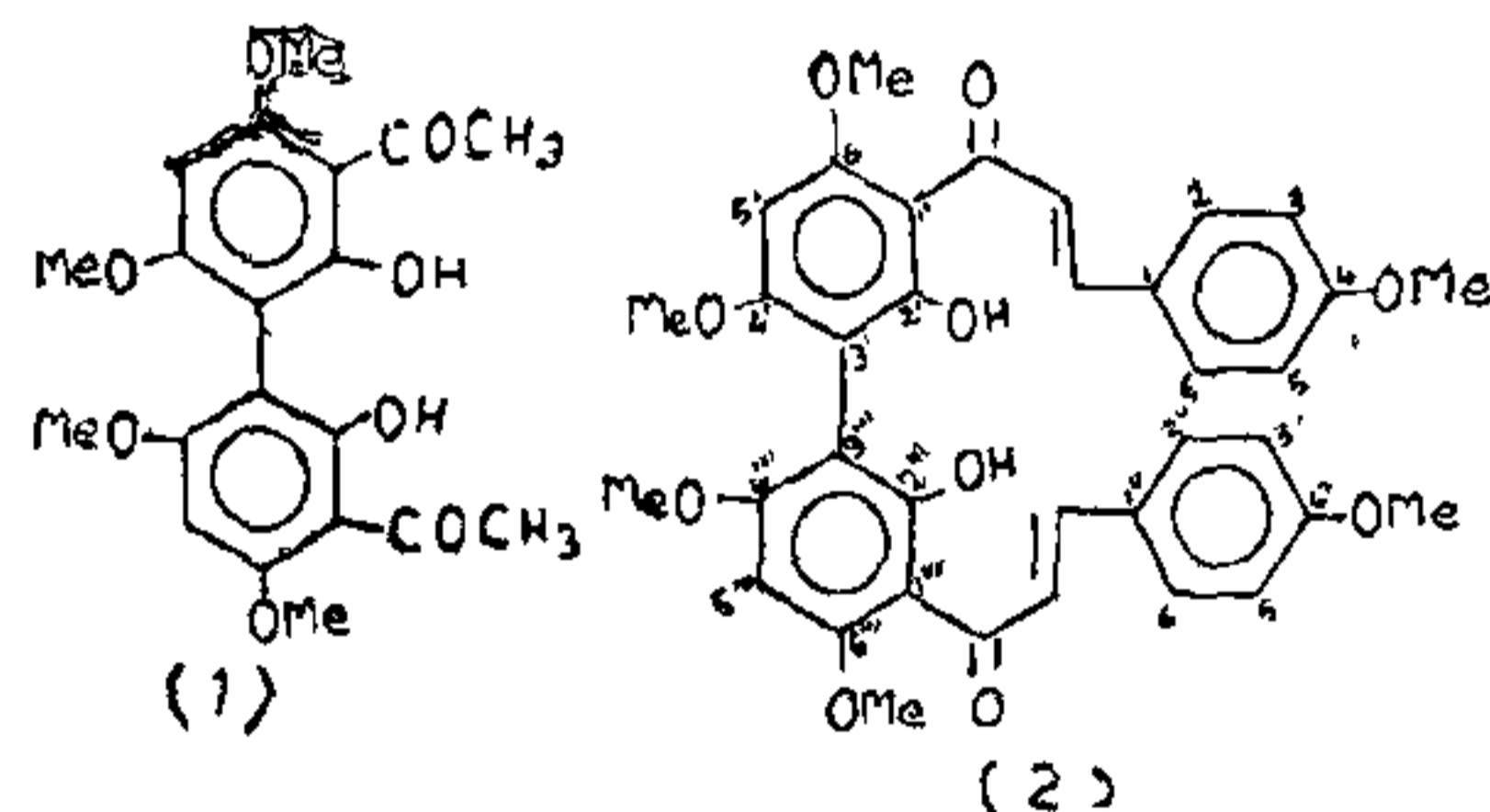


(1)

(2)

(3) R = OH

(4) R = OCOCH$_3$

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## ON THE MECHANISM OF THE ELBS PEROXYDISULPHATE OXIDATION

THE kinetics of the Elbs oxidation of phenols by peroxydisulphate in alkaline medium has been investigated by Behrman[1,2] and it has been concluded[2] that it is difficult to decide whether the rate limiting attack by the peroxydisulphate ion on the phenoxide is at the oxygen or carbon atom. Behrman also concluded that the evidence from the Hammet plots[2] is not of great value in distinguishing the above two possible electrophilic attacks. We wish to report here the possible attack by a careful analysis of the kinetic data.

In the case of p-halogenophenols, the rate of oxidation of p-fluorophenol is almost twice than that observed for phenol and the rates of oxidation of p-bromo- and p-iodophenols are lower. p-Chlorophenol has the same rate constant as that of phenol (Table I). The observed rate constants cannot be explained on the basis of + M effect of the halogen atoms though this effect is in the order p-F > p-Cl > p-Br > p-I. If this effect is important, then the rate constants of all the p-halogenophenols should be higher than phenol. A clue as to the possible site of attack as well as an explanation for the observed reactivities may be obtained if we take into account the possible d-orbital resonance in the case of p-chloro-, p-bromo and p-iodophenols. It has been well established by Baliah and co-workers[3–5] that chlorine, bromine and iodine can expand their valence shells by the utilization of their vacant d-orbitals. Such a d-orbital resonance becomes significant when electron-donating groups are present para to the halogen atom (Cl, Br, or I). In the Elbs oxidation, phenoxide ion is present and due to the d-orbital participation p-bromo- and p-iodophenoxides receive a significant contribution from structure A, which will reduce the



$$O = \langle \rangle = X^- \qquad X = Cl, Br \text{ or } I$$

A
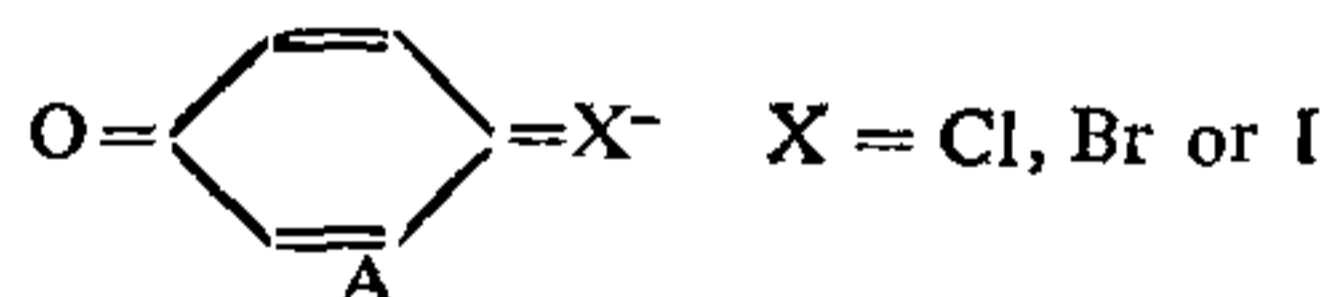
electron density at oxygen. In p-fluorophenoxide such a dπ-bonding is not possible and due to the + M

TABLE I

*The effect of substituents on the rate of oxidation of phenol[a]*

| Phenol | $k_2$,1-/mol-min | Phenol | $k_2$,1/mol min. |
|---|---|---|---|
| Phenol | 1·16±0·00 | m-Fluorophenol | 0·752±0·003 |
| p-Fluorophenol | 2·42±0·01 | m-Chlorophenol | 0·350±0·004 |
| p-Chlorophenol | 1·17±0·04 | m Bromophenol | 0·383 |
| p-Bromophenol | 0·970±0·04 | m-Iodophenol | 0·398 |
| p-Iodophenol | 1·05±0·00 | m-Methoxyphenol | 2·55±0·1 |
| p-Methoxyphenol | 20·6±1·0 | m-Methylphenol | 1·44±0·06 |
| p-Methylphenol | 5·62±0·05 | m-Cyanophenol | 0·225±0·003 |
| p-Cyanophenol | 0·140 | m-Carboxyphenol | 0·327±0·009 |
| p-Carboxyphenol | 0·155±0·005 | 2, 6-di-t-Butylphenol* | 31·0±0·5 |

[a] General conditions; Phenol-peroxydisulphate ratio = 10; 1·7 M KOH    Temperature 30°.

* In the case of 2, 6 di-t-butylphenol, 0·85 M KOH, 40% dioxane under nitrogen. All the values are taken from reference 2.