

the molecular chain. The association factors evaluated here are in general agreement with those reported earlier.

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SYNTHESIS OF 5,6-DIHYDROXY-7,4'-DIMETHOXYFLAVONE BY TRANSACYLATION METHOD

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In continuation of our work on the synthesis of partial methyl ethers of flavones¹ by transacylation method, we now report here the synthesis of 5,6-dihydroxy-7,4'-dimethoxyflavone (I) from the readily accessible scutellarein (5,6,7,4'-tetrahydroxyflavone) (II) by transacylation method². The flavone, I, had earlier been synthesised³ by Allan-Robinson method and known to occur in *Nepeta hindustana*⁴, *Galeopsis ladanum*⁵ and as 6-glucoside in the seeds of

*Catalpa ovata*⁶ and in the leaves of *Angelonia grandiflora*⁷.

Scutellarein⁸ (II) was fully benzoylated and the tetrabenzoylscutellarein (III) on reaction with two mols of dry phenol in the presence of silver carbonate and pyridine yielded 5,6-dibenzoyloxy-7,4'-dihydroxyflavone (IV). Methylation of IV with an ethereal solution of diazomethane afforded 5,6-dibenzoyloxy-7,4'-dimethoxyflavone (V), which on saponification yielded I. The synthetic product was identical with natural I (melting point, colour reactions and spectral data⁷) and the identity confirmed by direct comparison (co-PC) with an authentic sample from *Angelonia grandiflora*⁷.

5,6-Dibenzoyloxy-7,4'-dihydroxyflavone (IV)

5,6,7,4'-Tetrabenzoxyflavone (tetrabenzoylscutellarein) (III) (3 g), silver carbonate (1 g), phenol (0.75 ml) and dry pyridine (15 ml) were stirred for 3 h with exclusion of light and moisture at room temperature. The reaction mixture was treated with perchloric acid (20%, 100 ml) and the product IV crystallised from acetone-methanol, (1.8 g), m.p. 256–57°. It gave no ferric colour; UV (MeOH): 275, 333, 374 sh nm; + NaOAc: 277, 370 nm; + NaOMe: 275, 390 nm; + AlCl₃: 287, 333, 374 sh nm; IR (KBr): 3320 (br), 1730, 1650, 1600, 1370, 1260, 1220, 1100, 1080, 1060, 820 and 700 cm⁻¹.

5,6-Dibenzoyloxy-7,4'-dimethoxyflavone (V)

To an ether solution of compound IV (1.5 g), an excess of ethereal solution of diazomethane was added and 5,6-dibenzoyloxy-7,4'-dimethoxyflavone (V) crystallised from methanol as pale brown powder (1 g), m.p. 238–39° (d), IR (KBr): 3010, 2900, 1730, 1650, 1600, 1490, 1440, 1350, 1290, 1190, 1110, 1060, 1010 and 830 cm⁻¹.

5,6-Dihydroxy-7,4'-dimethoxyflavone (I)

Saponification of V with sodium methoxide afforded I, which crystallised from methanol-acetone as pale yellow needles, (0.1 g), m.p. 213–14° (lit⁷, 214–15°). It gave a positive ferric colour, green colour with sodium hydroxide, and was purple under UV and UV/NH₃; UV (MeOH): 270, 330 nm; + NaOAc: 270, 332 nm; + NaOMe: 275, 330 nm; + AlCl₃: 277, 304, 370 nm; IR (KBr): 3220, 2910,

1650, 1590, 1490, 1340, 1230, 1170, 1000, 900, 830 and 760 cm^{-1} .

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REVISED STRUCTURE OF A PRODUCT OF THE REACTION OF DIMEDONE WITH PHENYLGLYOXYLIC ACID

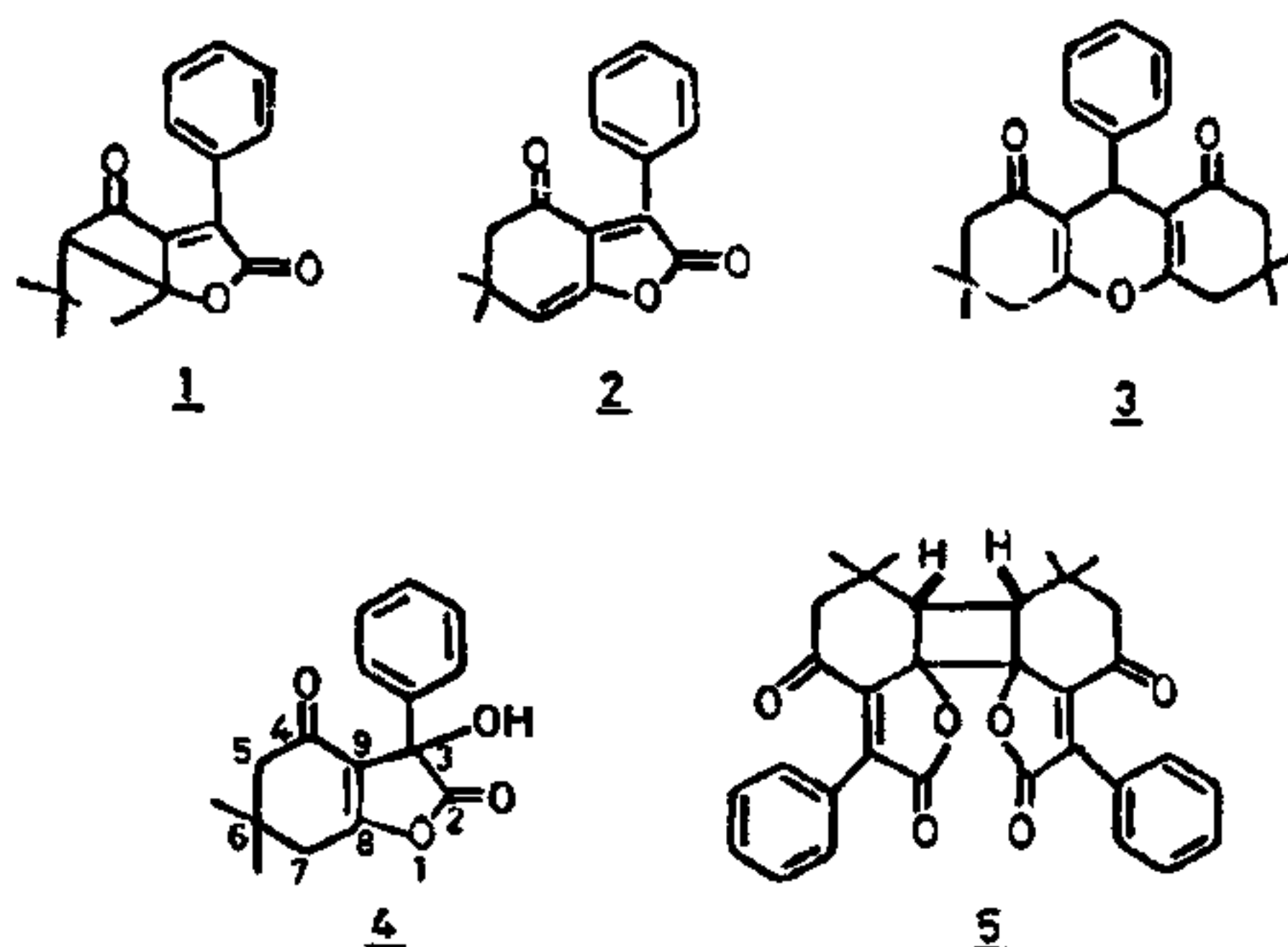
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STRUCTURE (1) was assigned¹ to one of the three products, m.p. 225–27°, obtained in the reaction of dimedone with phenylglyoxylic acid, the others being 2 and 3. The reaction leads initially to the hydroxylactone (4) which was not isolated. 2 could arise from 4 by dehydration and it was speculated that 1 could arise from 4 by addition of the carbanion next to the carbonyl group to C₈.

While the spectral properties agreed with structure (1), the highly strained formulation led us to reinvestigate the compound. The EI-MS showed M⁺ at 254 in agreement with structure (1) but the



FD-MS showed M⁺ at m/z 508 showing it to be a dimer. Compound 2 was recovered on heating at 140° for 16 h but was dimerised on irradiation at 350 nm in methanol solution to yield 5 quantitatively. The dimerisation is light-induced, not thermal. As expected², the head to head linkage is favoured by the use of a polar solvent. The singlet signal at δ 2.7 ppm in the PMR spectrum of 5 is assigned to the cyclobutane hydrogens. However, on the basis of the PMR and ¹³C NMR spectra a choice could not be made between different possible modes of dimerization of 2. In order to arrive at the structure and the stereo-chemistry, the compound was subjected to a single crystal X-ray diffraction study. A crystal of dimensions 0.03 × 0.60 × 0.70 mm was used for data collection on a CAD 4F-11 M diffractometer. $a = 12.270(2)$, $b = 18.293(3)$, $c = 13.729(1)$ Å; $\beta = 109.87$ (1)°; space group $P 2_1/a$ with $Z = 4$. The structure was solved by direct methods using MULTAN-78³ and refined using full matrix to a current R of 0.079 for 1230 observed reflections. The structure is represented by formula (5). The molecule has a solvent methylene dichloride molecule in the crystal structure.

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