

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

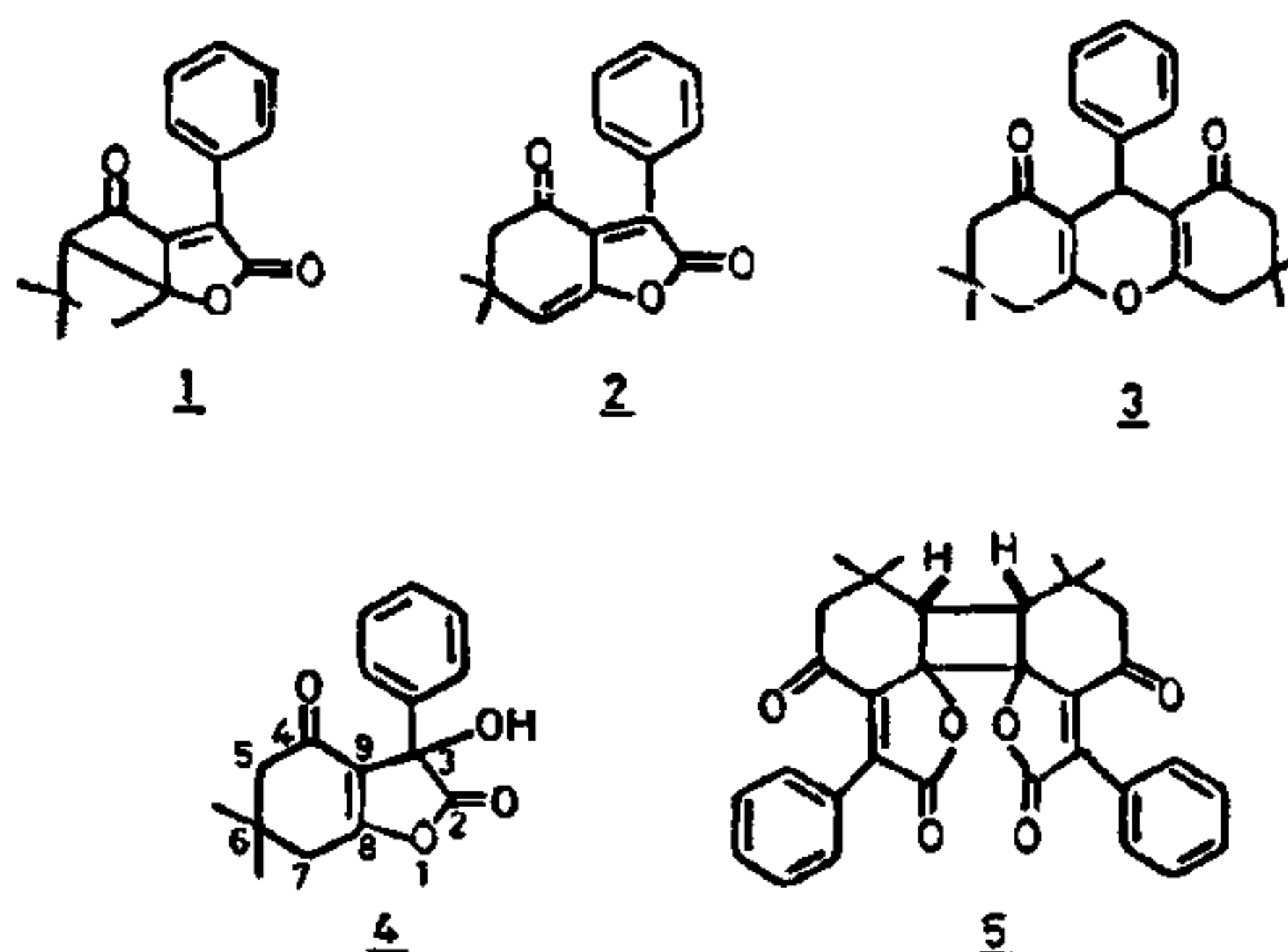
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STRUCTURE (1) was assigned¹ to one of the three products, m.p. 225–27°, obtained in the reaction of dimedone with phenylglyoxylic acid, the others being 2 and 3. The reaction leads initially to the hydroxylactone (4) which was not isolated. 2 could 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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EFFECT OF EXOGENOUS TREATMENT WITH SOME PHENOLIC COMPOUNDS ON NITROGEN FIXATION, GROWTH AND YIELD IN *CICER ARIETINUM* L. (CHICKPEA)

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PHENOLIC compounds, which are generally the secondary plant products, have recently come to limelight as regulators of many physiological processes. However, reports of the effect of phenolic compounds on symbiotic nitrogen fixation are scanty. It was therefore, considered worthwhile, to initiate these studies on the effect of some phenolic substances on symbiotic nitrogen fixation in *Cicer arietinum* L. (Chickpea) cv. C-235 (seeds procured from the Haryana Agricultural University, Hisar). Two hundred earthenware pots (25 cm dia.) were filled with a mixture of thoroughly powdered garden loam, sand and farm yard manure in the proportion of 3:1:1 by volume. Ten seeds were sown in each pot. The seedlings were inoculated with appropriate rhizobial strains. After thinning, three plants were left in each pot. The pots were divided into five equal lots. The plants in each lot were treated as follows: (i) a monophenol, vanillic acid; (ii) monophenol, salicylic acid; (iii) a diphenol, caffeic acid; (iv) a polyphenol, chlorogenic acid, and (v) distilled water to serve as untreated control. Aqueous suspensions of each of the phenols at a concentration of 10^{-4} M were made afresh during treatment. The concentrations used, were selected on the basis of preliminary trials made earlier. The plants were treated on the basis of dispensing five drops each of the above solutions on each cotton wad placed at the apices of the plants. The applications with the various solutions were made thrice during a day. Two successive treatments were made in the same manner, the first at 40 days after sowing and the second, 10 days after the first set of treatments. The

effects of phenolic compounds on some important enzymes namely IAA oxidase, peroxidase and polyphenol oxidase were studied. The IAA oxidase assay was carried out on nodule extracts using the colour reaction by modified salkowski reagent¹. Peroxidase activity was measured² by using *o*-dianisidine in the presence of H₂O₂. The activity of polyphenol oxidase was estimated by using catechol in 80% alcohol as substrate³. The rate of nitrogen fixation was determined by the acetylene reduction bioassay⁴. The effect of various phenolic treatments on the number and dry weight of nodules was studied to express their effect on plant growth.

With the application of two monophenols, vanillic acid and salicylic acid, there was a well marked reduction in the number and dry weight of nodules (table 1), which became more pronounced with time. The application of diphenol, caffeic acid and polyphenol, chlorogenic acid resulted in an increase in the number and dry weight of nodules. Chlorogenic acid application was the most promotive showing 30% increase after 80 days and 100% after 110 days.

The rate of nitrogen fixation (table 2) showed considerable reduction with the application of two monophenols, while the other phenols, especially chlorogenic acid, resulted in an enhancement of this activity.

Phenolic compounds released from root exudates, leaf leachate and decaying organic matter have been

Table 1 Effect of different phenolic compounds on nodule numbers/dry weight (g/plant) in chickpea

Days after sowing	Treatments				
	DW	VAN	SAL	CAF	CHLOR
80	76/0.10	66/0.09	61/0.09	88/0.11	84/0.13
110	85/0.12	49/0.08	47/0.08	105/0.15	115/0.25

DW, Distilled water; VAN, Vanillic acid; SAL, Salicylic acid; CAF, Caffeic acid, and CHLOR, Chlorogenic acid.

Table 2 Effect of different phenolic compounds on rate of nitrogen fixation (m. moles ethylene/mg nodule dry wt./h) in the nodules of chickpea

Days after sowing	Treatments				
	DW	VAN	SAL	CAF	CHLOR
95	66	54	41	116	114
125	23	15	18	34	38

DW, Distilled water; VAN, Vanillic acid; SAL, Salicylic acid; CAF, Caffeic acid, and CHLOR, Chlorogenic acid.