

(1) 2 (2'-Furyl) 4, 6-dimethyl benzothiazolyl hydrazine.

The preliminary trials on germination show that (C) and (E) are not so effective. On the strength of these germination experiments, field trials of these compounds were undertaken, along with control and gibberellic acid* as a standard. All solutions were of 5 ppm dilution. Forty seeds of *Cicer arietinum* were soaked in 100 ml solution of each compound for five hours. The seeds were sown in earthen pots and arranged in randomized block design, in three rows with nine treatments. On 5th day 100% germination was found in control whereas in standard it was only 80%. On 25th day nodulation was initiated. Three plants from each pot were removed at interval of 7 days for nodule count. In all five observations were made till crop attained the preflowering phase, when the experiment was terminated. Treatments with (A), (B) and (D) were having more or less the same number of nodules as in standard whereas the nodulation was better than control and standard with (F), (G), (H) and (I). This clearly showed that naphthalene ring prevented the nodule formation whereas electron donating methyl groups on benzonucleus stimulates the nodulation provided it is a uncyclized compound or having a mercapto substituent at 3 position in cyclic system. Even in germination result the compounds (F) and (G) were found to be superior.

The results on number of nodules in the different treatments (Table I) show that (F), (G), (H) are statistically significant at 5% whereas (F) and (G) results are statistically significant even at 1% at 12 df. (A) and (B) seem to have retardatory effect on nodule formation.

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* Known plant growth regulator, used in earlier references.

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TAUTOMERISM OF 2-HYDROXY CHROMONES AND 4-HYDROXYCOUMARINS

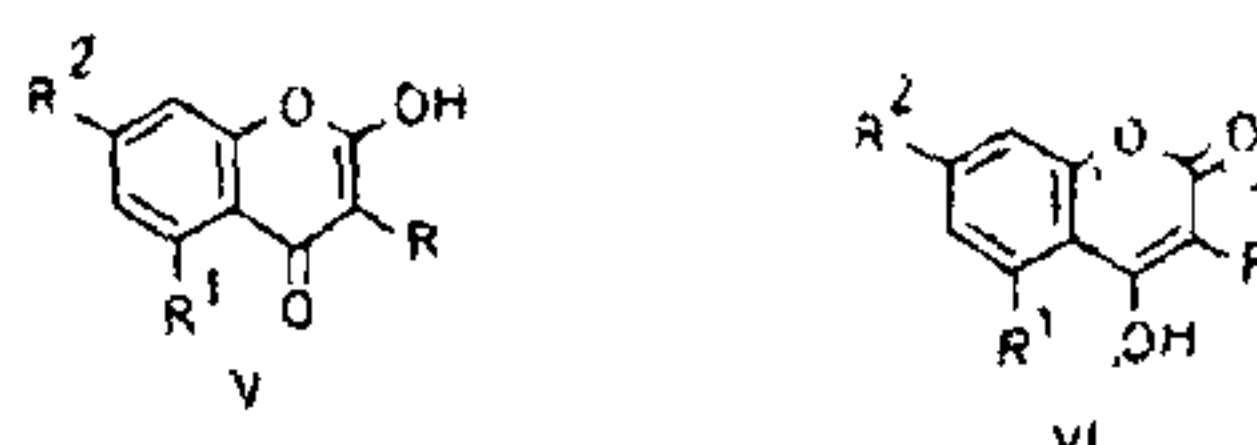
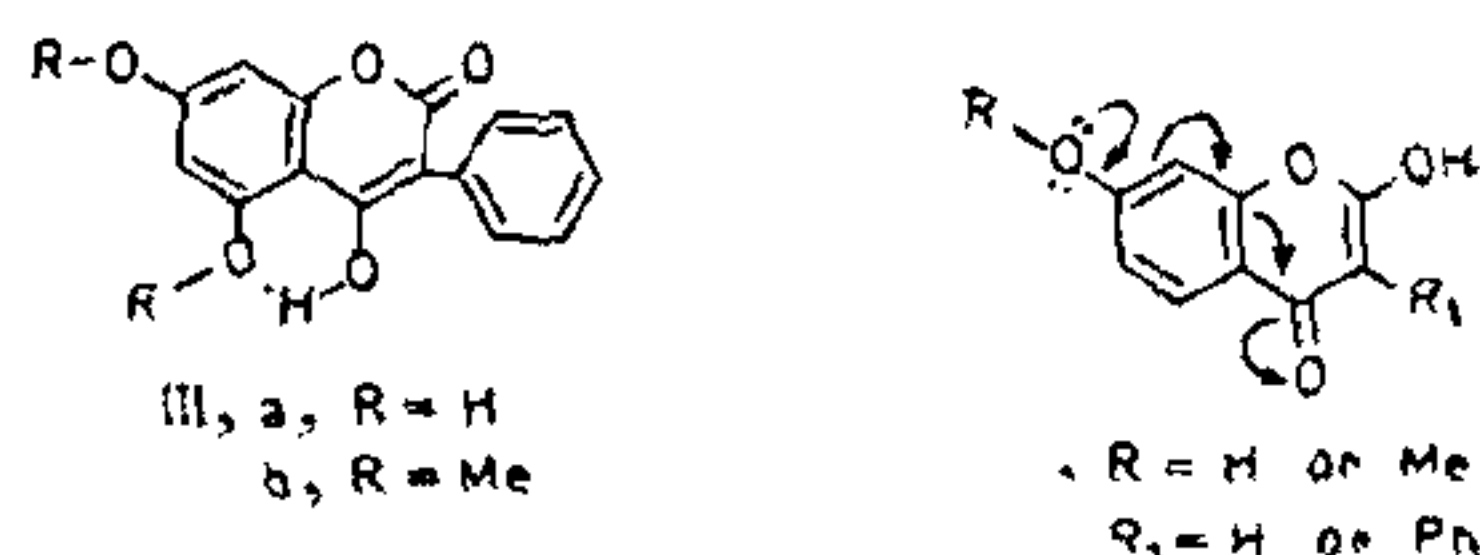
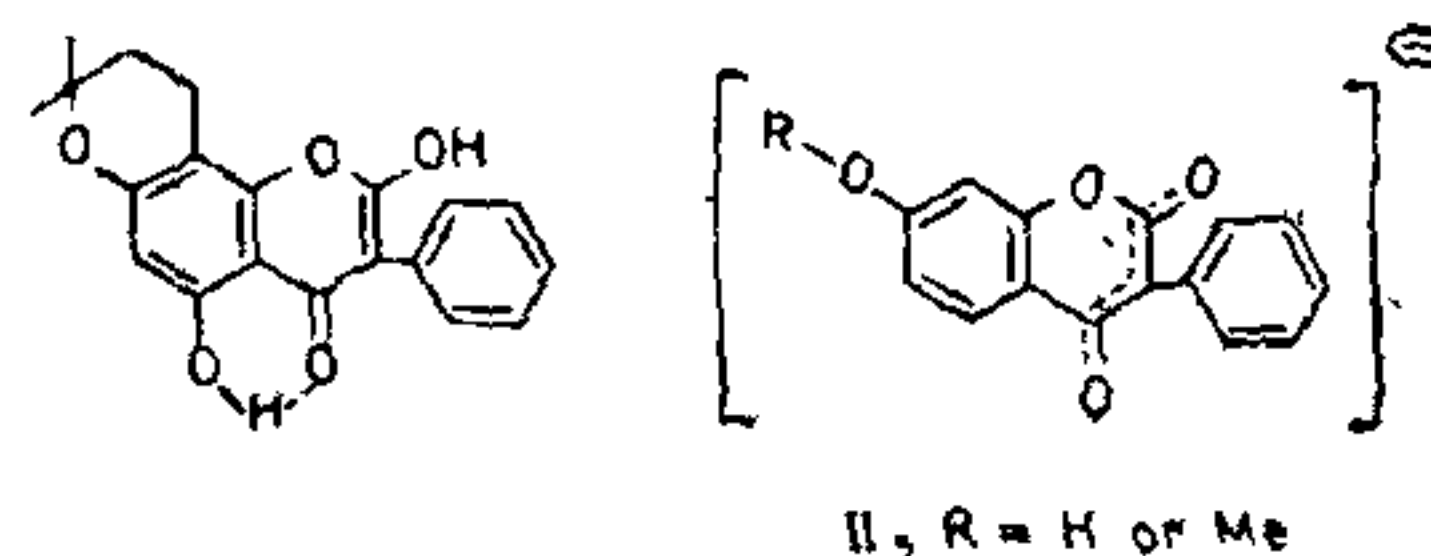
4-HYDROXYCOUMARINS and 2-hydroxychromones/2-hydroxyisoflavones exist as tautomers. As to which of the tautomer is thermodynamically more stable has been shown to depend upon the substitution pattern. In the present communication guidelines

for predicting the stability of tautomers with different substitution pattern and explanation for the same are given.

From study of the IR spectra of 4-methoxycoumarin and 2-methoxychromone it was shown by Knobloch and Prochazka¹ that the coumarins absorb at about 1712 cm^{-1} and the chromones at about 1645 cm^{-1} . On this basis they deduced a coumarin structure for 4-hydroxycoumarin ($\nu_{\text{C=O}} 1708\text{ cm}^{-1}$, solid) but a chromone structure for dicoumarol ($\nu_{\text{C=O}} 1650\text{ cm}^{-1}$, solid). The formation of the former has been attributed to the more facile enolisation of ketonic carbonyl in 4-position than the ester carbonyl in 2-position.

Johnson and Pelter^{2,3} on the basis of IR spectra of 3-phenyl-5-hydroxy derivative (I, $\nu_{\text{C=O}} 1640\text{ cm}^{-1}$) showed that the isoflavone structure is preferred over the corresponding coumarin tautomer due to hydrogen bonding between 5-hydroxyl and 4-carbonyl groupings. In the case of 5-methoxy derivatives such a bonding is not possible and therefore the coumarin structure ($\nu_{\text{C=O}} 1704\text{ cm}^{-1}$) is more stable.

According to Subba Rao *et al*⁴ 3-phenyl-4-hydroxy- and 3-phenyl-4, 5-dihydroxycoumarins are more stable as compared to their corresponding isoflavones and have attributed the low frequency absorption ($\nu_{\text{C=O}} 1645\text{ cm}^{-1}$) of carbonyl group of the former, to the existence of a dianion state (II). In the latter hydrogen bonding (III a, b) between C₄-hydroxyl and C₅-hydroxyl or methoxyl prevents the formation of a dianion and therefore it absorbs at a higher frequency ($\nu_{\text{C=O}} 1700\text{ cm}^{-1}$) as for coumarins.



- a, R = R¹ = H, R² = OH
- b, R = Ph, R¹ = H, R² = OH
- c, R = Ph, R¹ = H, R² = OMe
- d, R = Ph, R¹ = R² = OH
- e, R = H, R¹ = R² = OH

- a, R = H, R¹ = R² = OMe
- b, R = Ph, R¹ = R² = OMe
- c, R = OMe, R¹ = H, R² = OH
- d, R¹ = H, R = R² = OMe
- e, R = R¹ = R² = OMe

The existence of a dianion state as envisaged by Subba Rao is unlikely because in that case the IR spectra should show two carbonyl bands due to the different electronic environment about the two carbonyl groups. However, the IR spectra of different compounds (Table I) in KBr shows only one carbonyl absorption either at about 1650 cm⁻¹ or 1710 cm⁻¹ corresponding to the chromone/isoflavone and coumarin structures respectively.

TABLE I

Compound No.	Substitution pattern	>C=O absorption (cm ⁻¹)	Stable tautomer
1	2, 7-dihydroxy ⁵ (V a)	1667	Chromone
2	3-Phenyl-2, 7-dihydroxy (V b)	1639	Isoflavone
3	3-Phenyl-2-hydroxy-7-methoxy (V c)	1653	Isoflavone
4	3-Phenyl-2, 5, 7-tri-hydroxy (V d)	1630	Isoflavone
5	2, 5, 7-Trihydroxy (V e)	1650	Chromone
6	4-Hydroxy-5, 7-dimethoxy (VI d)	1720	Coumarin
7	3-Phenyl-4-hydroxy-5, 7-dimethoxy (VI e)	1704	Coumarin
8	3-Methoxy-4, 7-dihydroxy (VI c)	1695	Coumarin
9	4-Hydroxy-3, 7-dimethoxy (VI d)	1690	Coumarin
10	4-Hydroxy-3, 5, 7-trimethoxy (VI e)	1700	Coumarin

Guidelines for predicting the stability of tautomers having hydroxyl or methoxyl in 3, 5 and 7 positions are as follows:

A hydroxy or methoxy group at 7-position, being in conjugation with the C₄-carbonyl through the benzene ring stabilises the 2-hydroxyisoflavone/2-hydroxychromone tautomers as shown in structure (IV) due to the enolization of 2-carbonyl. However, presence of a methoxy group at 3-position feeds the electrons in the direction opposite to that caused by 7-hydroxyl, thus preventing the resonance stabilization of 4-carbonyl. Therefore 3-methoxy derivatives show IR absorption characteristic of coumarins. Thus 2, 7-dihydroxychromone (V a, 1667 cm⁻¹), 2, 7-dihydroxyisoflavone (V b, 1639 cm⁻¹) and 2-hydroxy-7-methoxyisoflavone (V c, 1653 cm⁻¹) are more stable as compared to the corresponding coumarins, whereas 3-methoxy-4, 7-dihydroxycoumarin (VI c), 4-hydroxy-3, 7-dimethoxycoumarin (VI d) and

4-hydroxy-3, 5, 7-trimethoxycoumarin (VI e) have characteristic carbonyl frequency at ν_{\max} 1695, 1690, 1700 cm⁻¹ respectively.

Hydroxyl at 5-position stabilises the isoflavones/chromones because of hydrogen bonding preferably with the carbonyl rather than the hydroxyl at 4-position. Whereas 5-methoxyl favours the coumarin structure because the 4-hydroxyl in that case is hydrogen bonded (III b). Hence 4-hydroxy-5, 7-dimethoxycoumarin (VI a, 1720 cm⁻¹), 3-phenyl-4-hydroxy-5, 7-dimethoxycoumarin (VI b, 1704 cm⁻¹) are more stable than the corresponding isoflavones while 2, 5, 7-trihydroxychromone (V e, 1650 cm⁻¹) and 2, 5, 7-trihydroxyisoflavone (V d, 1630 cm⁻¹) are energetically more favoured than the corresponding coumarins.

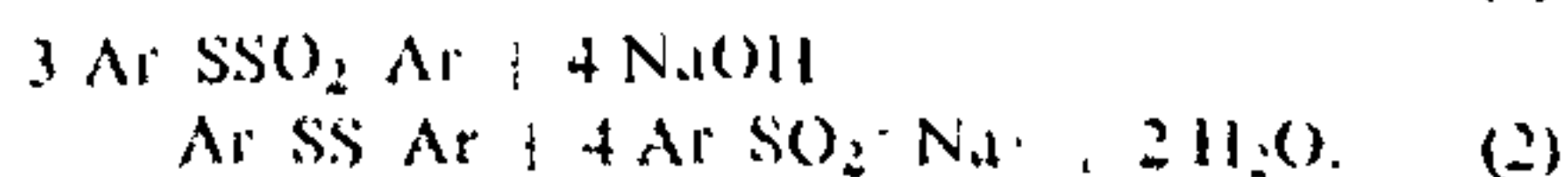
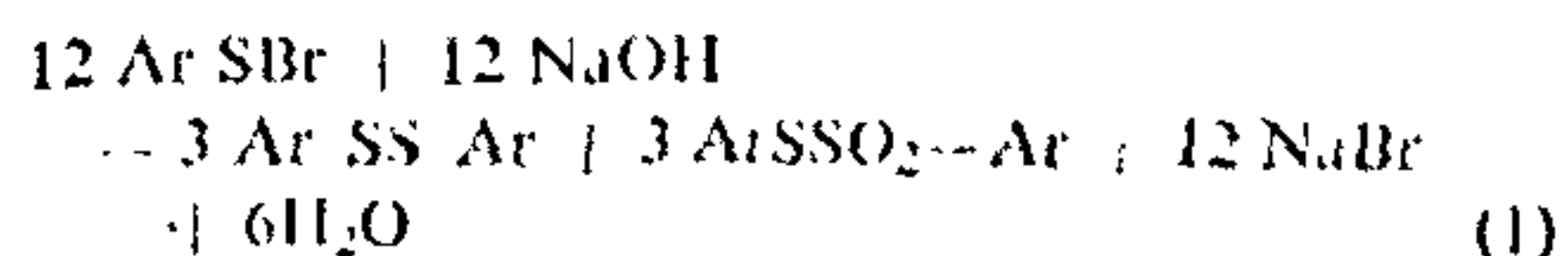
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ACTION OF ALKALI ON 2-*p*-TOLYLAZO-NAPHTHALENE-1-SULPHENYL BROMIDE

THE formation of monosulphide from sulphenyl bromides of orthomeraceto azo compounds in strongly alkaline medium, has not been reported so far¹⁻³. This note gives preliminary report of the formation of the corresponding monosulphide (VI) from the newly synthesized sulphenyl compound, 2-*p*-tolylazo-naphthalene-1-sulphenyl-bromide (II) under strongly alkaline conditions. Generally, the sulphenyl bromides of ortho-mercapto azo compounds react with an appreciable excess of alkali to give the precipitate of the corresponding disulphides and water soluble alkali sulphinates according to the equations (1, 2).



The thiolsulphonates initially formed react instantaneously with excess alkali to give more of disulphides and alkali sulphinates. We have synthesized new