STEREOCHEMISTRY OF GOSSYPOL

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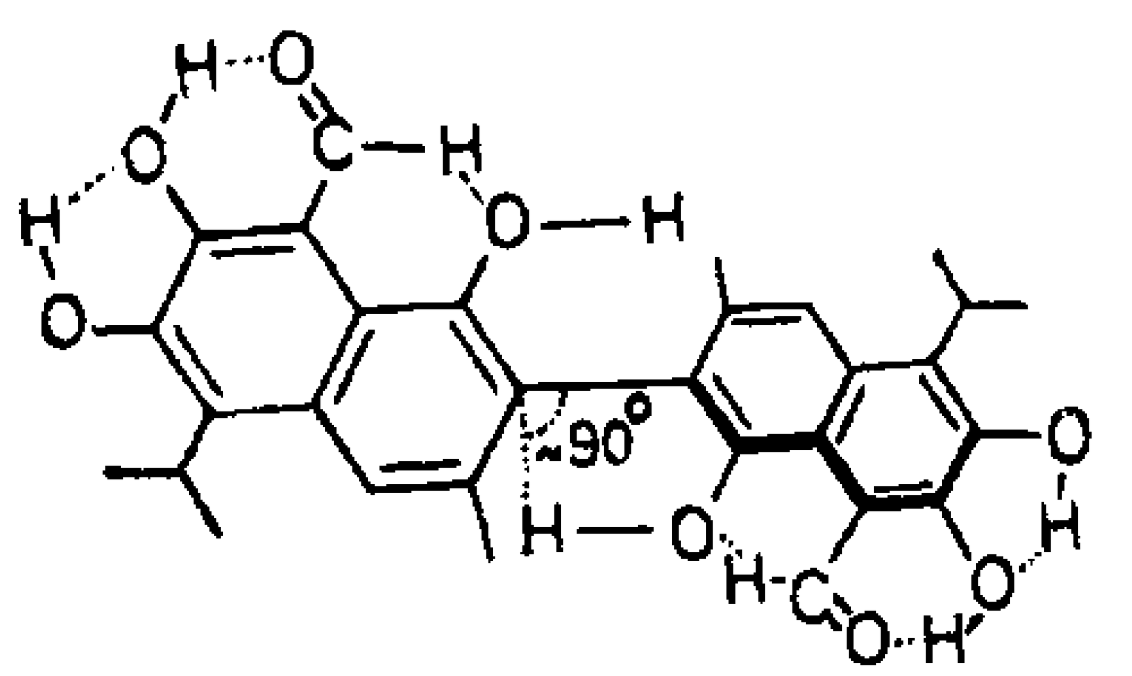
IN our earlier papers[1,2] relating to the study of (+) and (±) gossypol and their derivatives, useful information was given about the isolation of the different forms of gossypol methyl ethers and acetyl derivatives and about their structures derived from spectral data. Now it will be useful to consolidate the knowledge gained in relation to the understanding of the stereoisomerism of gossypol.

The gross structure of gossypol as a binaphthyl with substituents in the *o*-positions to the interlink indicated the possibility of steric hindrance and consequently of optical activity. The well-known examples of optically active biphenyls, binaphthyls and others having ortho substituents support the above expectation. This feature of steric hindrance in gossypol has been considered by Marckmann and Glushenkova[3], who have expressed the view that in gossypol the rings do not lie in one plane owing to steric hindrance and oscillate at a mean angle of 120°. Wood *et al.*[4] based on U.V. and I.R. studies of (±) gossypol in different solvent systems considered that the two naphthalene rings are in near perpendicular conformation and in inert solvents hydrogen bonding produces a rigid structure (I).



(I)

More recently in the Indo-Soviet Symposium on Natural Products[5] and in their paper[6] Sadykov *et al.* reported a study of (±) gossypol and its partial and complete methyl ethers using I.R. spectra in solid phase and in solution and NMR spectra in $CDCl_3$ and CF_3COOH separately; the data confirmed the presence of inter and intramolecular hydrogen bonds. The superposition and broadening of most of the signals indicated lack of free rotation about the 2, 2′-internaphthyl bond. Different samples of hexamethyl ether with different m.ps. showed differences in the methoxyl resonance signals indicating that they were not uniform; there were clusters of methoxyl signals with varying intensity ratios. Moreover, TLC always gave two spots. Purified samples showed NMR spectrum which was more homogeneous.

They concluded from these data that (±) gossypol and its dimethyl ether exist in the aldehydic form, whereas the tetra and hexamethyl ethers exist in the lactol ring form. For the latter they visualised the possibility of geometrical isomeric forms arising out of the disposition of the methoxyls at the lactol ring carbon atom.

In the same symposium our studies[7] on (+) gossypol derivatives and our detailed findings on the structure of gossypol were discussed. The discovery of (+) gossypol and the persistence of optical activity not only in its derivatives like the methyl ether, acetate and anil, but also in its degradation products, apogossypol and desapogossypol hexamethyl ethers are highly significant. In gossypol itself the activity could arise from (*i*) atropisomerism of the binaphthyl system and (*ii*) from the asymmetric carbon system of the lactol form. Since the activity persists in the aldehyde forms of the gossypol derivatives and also in apogossypol and desapogossypol hexamethyl ethers, it follows that atropisomerism is the main cause. On the basis that the two naphthalene rings are nearly perpendicular to each other and without considering other influences, there can be only one (+) form, one (−) form and one (±) form. As mentioned earlier, this is so in the case of apogossypol hexamethyl ether and desapogossypol hexamethyl ether. The presence of aldehyde groups in gossypol and their capacity to form lactol rings can give rise to six forms in each case of (+), (−) and (±) gosspyols as shown in Fig. 1.

The validity of these forms has been corroborated by our experimental results reported in earlier papers[1,2] relating to the study of (+) and (±) gossypols and their derivatives. Two definite forms corresponding to two structures of (*i*) gossypol-A with two aldehyde groups and (*ii*) gossypol D or F having the same relative orientation of the lactol groups have been isolated from (+) gossypol in the form of their methyl ethers. Similarly two more forms are represented by the structure of gossypol-E in the form of its hexaacetate having the lactol groups differently oriented and gossypol B or C from (±) gossypol in the form of its hexamethyl ether with one aldehyde and one lactol

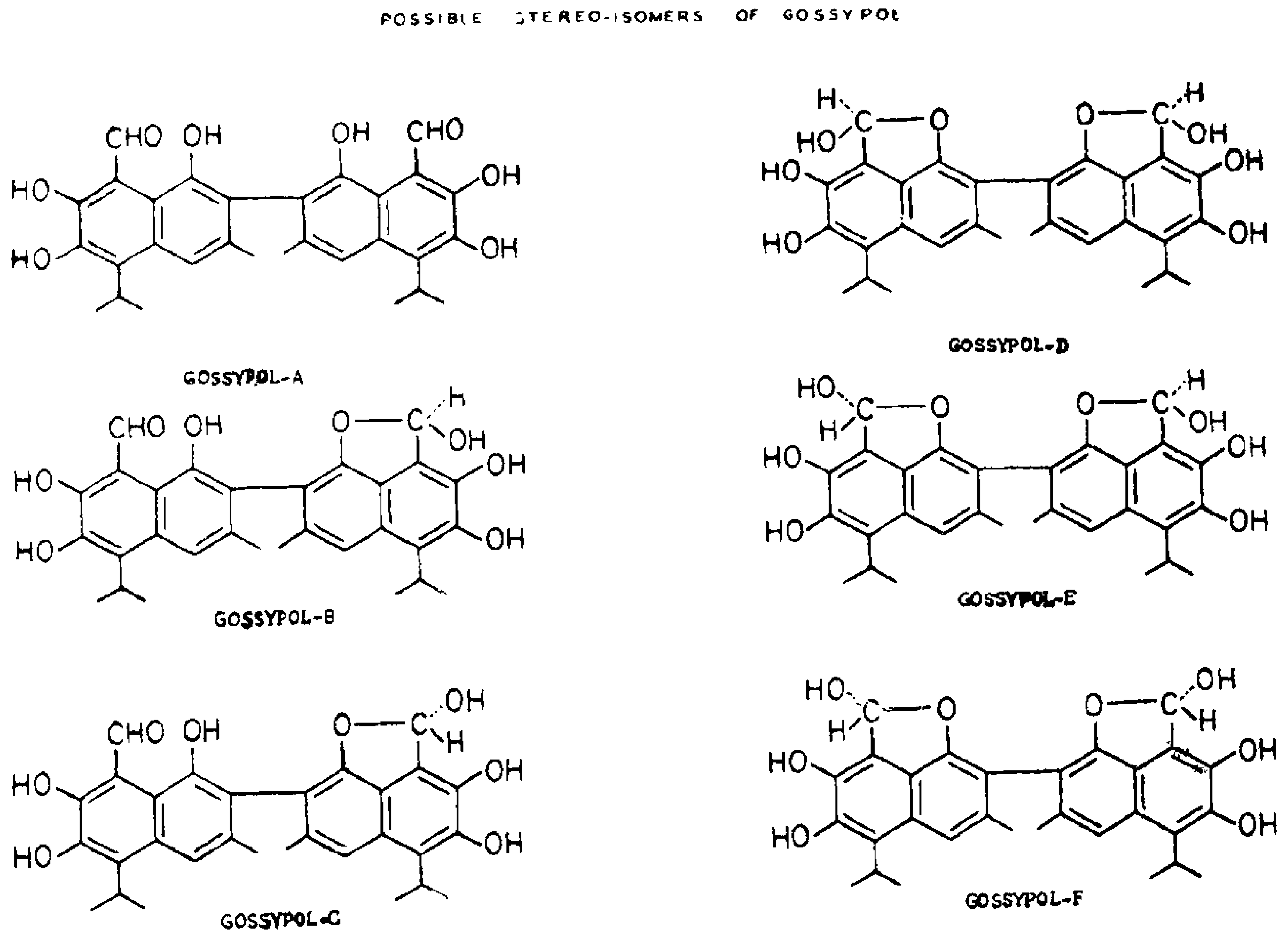


FIG. 1. Structures of different gossypols.

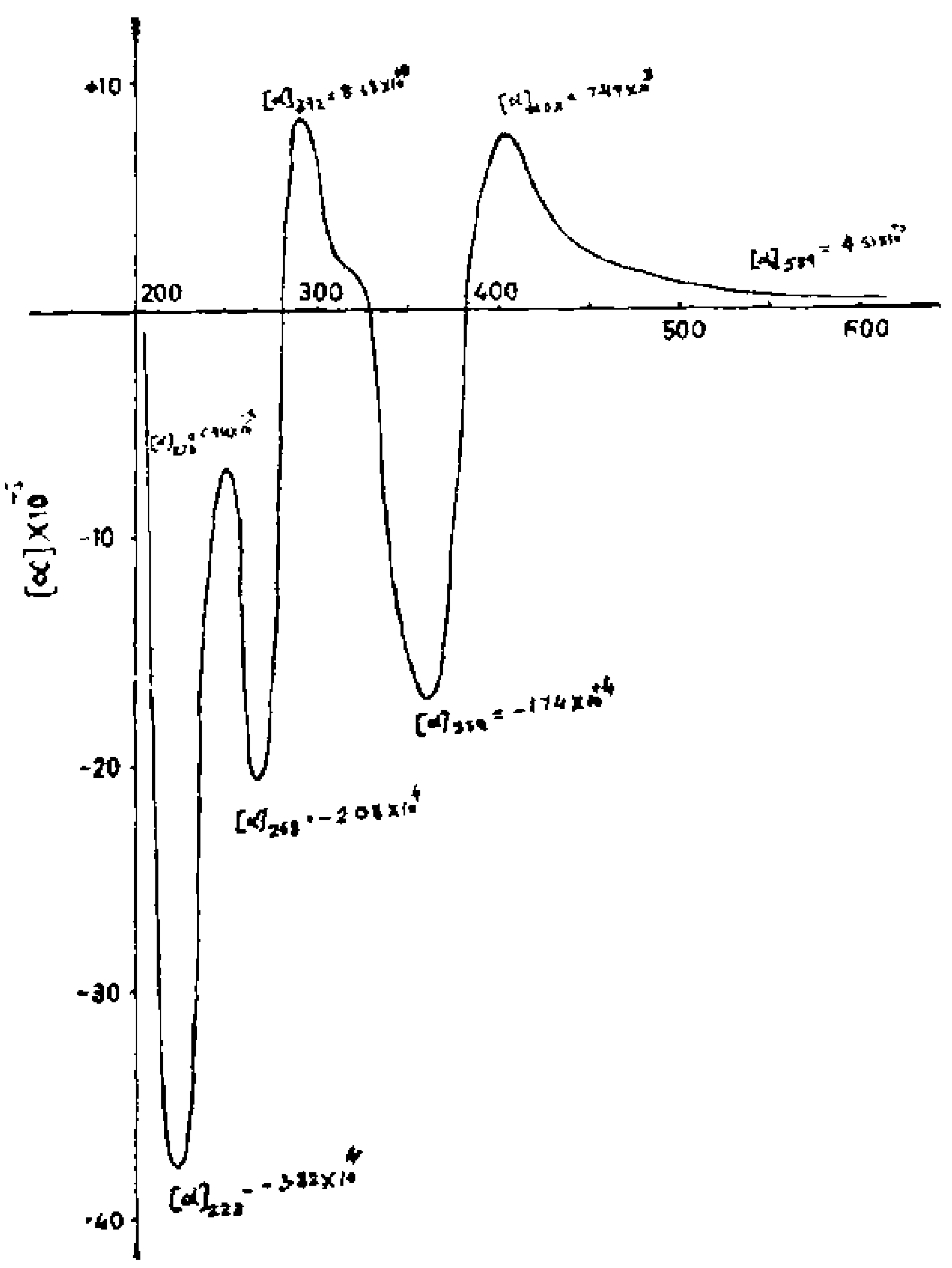


FIG. 2. ORD curve of (+) gossypol.

group. Further, the study of anils and their methyl ethers (details of which will be published later) support the above structures for gossypol. Thus totally four different structures of gossypol have been isolated and studied. Further work may bring experimental support for the other forms also.

No doubt, therefore, that gossypol is a mixture of different forms which are interchangeable. The composition can vary with the conditions of cyrstallisation and with the nature of the derivative such as methyl ether or acetate. This explains the variations, noted earlier, of melting points and crystal structures. Since the pigment has medicinal uses, its physiological effects may depend upon the predominant form in which it functions under the conditions of its use.

The absolute configuration of (+) gossypol cannot be solved fully with the information available at present. However, by analogy with the results of Djerrasi[8] on the absolute configuration of 1, 1′-binaphthyls in relation to their ORD curves, it may be concluded that (+) gossypol with positive cotton effect curve[1] in the long wavelength region may have the R configuration. The problem has yet to await the synthesis of certain model 2, 2'-binaphthyl compounds and determination of their absolute configuration by unambiguous methods such as X-ray diffraction method.

1. Datta, S. C., Murti, V. V. S. and Seshadri, T. R., *Indian J. Chem.* **1972**, **10**, 263.
2. —, — and —, *Ibid.* (In press).
3. Marckmann, A. L. and Glushenkova, A. I., *Chem. Abstrs.*, **1965**, **63**, 17995 *h*.
4. Wood, A. B., Robinson, F. V. and (Miss) Lago, R. C. A., *Chem. and Ind.*, 1969, No. 48, p. 1738.
5. Baram, N., Smailov, A. I., Leontyev, V., Kamaev, F. and Sadykov, A., *Indo Soviet Symposium on Natural Products*, Abst., Feb. 1970, p. 31.
6. —, —, —, — and —, *Dok. Acad. Sci.*, USSR, 1970, **195**, 1097.
7. Datta, S. C., *Indo-Soviet Symposium on Natural Products*, Abst., Feb. 1970, Part II, p. 117.
8. Djerassi, C., *J. Am. Chem. Soc.*, 1960, **82**, 4740.

INFLUENCE OF MOISTURE ON SOIL AGGREGATION

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Optimum Soil Moisture for Maximum Plant Growth and Crop Yield

HELLRIEGEL (1883) first demonstrated the relationship between the soil moisture and the final amount of plant growth by growing barley in sand cultures supplied with different amounts of water. The entire crop consisted of straw with the smallest amount of water, and with increasing amounts of water, the yields of both straw and grain passed through a maximum and then decreased; but the maximum yield of grain occurred with a smaller amount of water than did the maximum yield of straw[1,2]. In 1912, Widtsoe obtained similar results with wheat under field conditions and reported that the yield increased with increasing water supply, the straw more than the grain[1]. Traaen (1916) studied the effect of different percentages (3, 5, 10, 15, 17·5, 20 and 25) of moisture in the soil at 13° C and 25° C and found that maximum nitrate was formed with 17·5% moisture at 13° C at the end of 66 days[1].

Since the work of Hellriegel and of Widtsoe, it has been increasingly recognised that the optimum moisture content of soils is a most important factor in soil conditions and plant growth: *e.g.*, "Generally, however, 50 to 60% of the total moisture holding capacity of the soil is optimum for the majority of cultivated crops"[3]; "Considered in relation to both microbial activities and crop growth, the optimum water content of soils is at about two-thirds saturation, leaving one-third of the pore space to be occupied by air"[4]. Additional supplies of water may sometimes be advantageous depending on the nature of crops and other conditions, may sometimes be ineffective and sometimes be harmful[1].

Recently Dakshinamurti and Reddy (1971)[5] conducted field experiments on alluvial soil, irrigating two varieties of wheat at six levels, *viz.*, ½, ¾, 1, 1½, 2 and 3 times field capacity. They obtained the highest yields of grain with both the varieties of wheat on the soil irrigated with water between ¾ and 1 field capacity. They stated that if the irrigation schedules were restricted to ¾ field capacity to one field capacity, most of the mineralisable nitrogen would be available to the roots resulting in maximisation of yields.

Earlier Studies on Soil Moisture

Moisture and Soil Aggregating Effect of Organic Residues.—In the course of their studies on the influence of temperature (10°, 25°, 40° and 55° C) and moisture (25, 50, 75 and 100%) on the soil aggregating effect of organic residues such as alfalfa-grass, hay tops, blood meal, wheat straw, sawdust, cow manure and sucrose for various periods (5, 10, 20, 50 and 100 days), Martin and Craggs (1946)[6] found that greatest over-all aggregation occurred in the soil samples maintained at 25% moisture, that slightly less beneficial action resulted in the series kept at 50 and 75% moisture, and that in the soil kept saturated with water, there was a great reduction in the aggregating effect.

Alderfer (1946)[7] conducted aggregating studies on plots of Hagerstown silt loam surface soil which had been subject to 5 years of each of the following annual treatments: barnyard manure, wheat straw, corn stover, a ryegrass cover crop, and a 4–12–8 fertiliser were incorporated in the surface soil. Soil moisture content was closely related to the amount and size of water stable aggregates when the soil was analysed in its field-moist condition. The effect of soil moisture content was modified, however, by seasonal conditions such as alternate wetting and