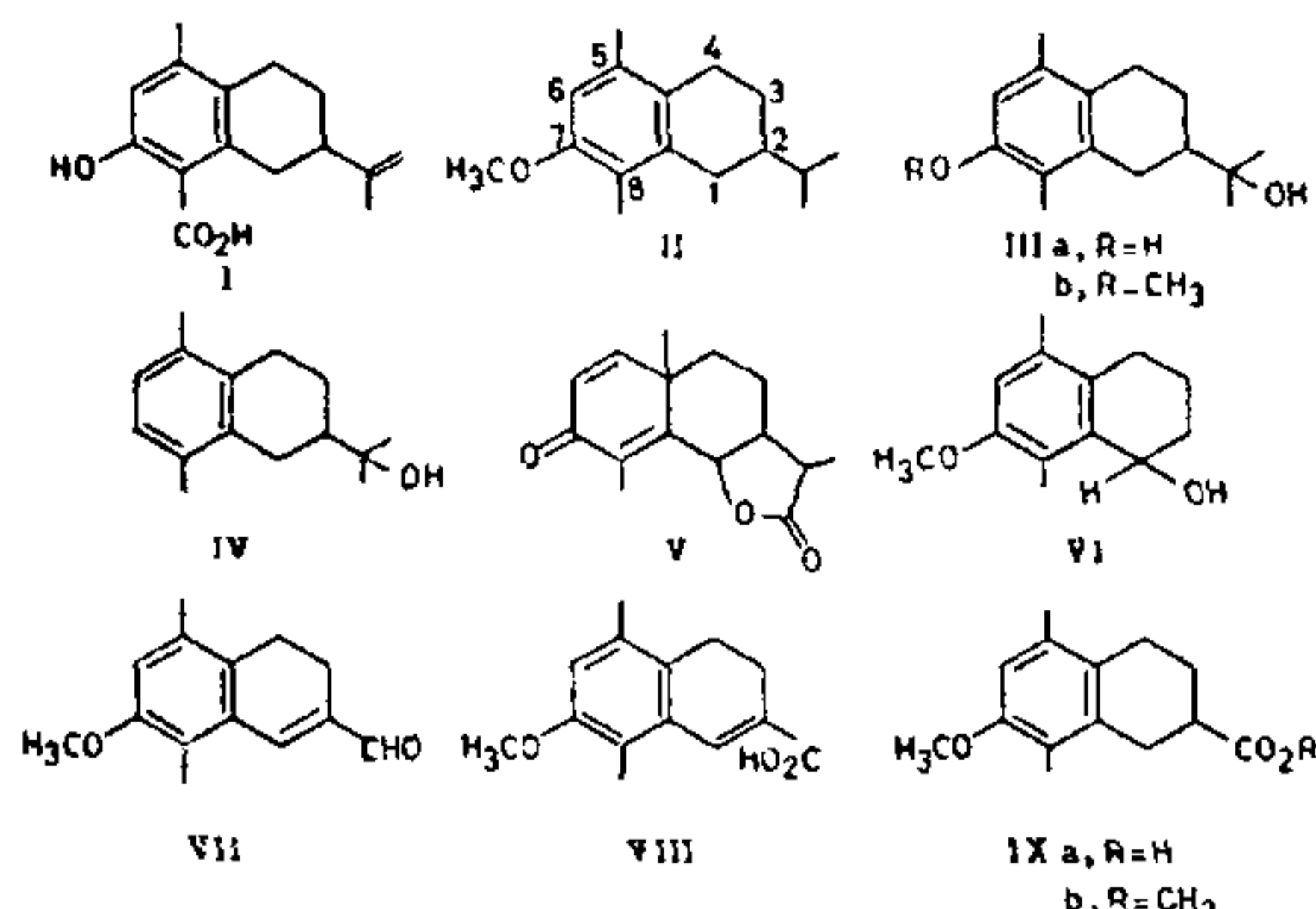


**SYNTHESIS OF 7-METHOXYOCCIDOL  
[2-(2'-HYDROXYISOPROPYL)-7-METHOXY-  
5,8-DIMETHYL-1,2,3,4-TETRAHYDRONAPHTHA-  
LENE]. A BIO-CONGENER OF OCCIDOL**

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THE recent isolation<sup>1</sup> of the moderately antileukaemic sesquiterpene aromatic hydroxy acid, manicol(I) from *Dulacia guinensis* and its structure elucidation by correlation with 2-isopropyl-7-methoxy-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene (II) prompted us to report our work<sup>2</sup> on the closely related title compound (IIIb), the synthesis of which was primarily undertaken to obtain the 7-methoxy congener of the naturally occurring occidol<sup>3,4</sup> (IV) on the assumption that in some plant source in nature dienones structurally related to santonin (V) could give rise to the 7-hydroxy analogue (IIIa) of occidol by the well-known dienone-phenol rearrangement, followed by other biogenetically plausible steps.

7-Methoxy-5,8-dimethyl-3,4-dihydro-2-naphthaldehyde<sup>5</sup> (VII), obtained from 7-methoxy-5,8-dimethyl-1-tetralol (VI) by Vilsmeier reaction, was oxidized to the corresponding acid (VIII) by Jones reagent<sup>6</sup> and hydrogenated (Pd/C, 10%) to afford the tetralin carboxylic acid (IXa). Its methyl ester (IXb) gave on Grignard reaction with methylmagnesium iodide 7-methoxyoccidol (IIIb), the title compound. The PMR characteristics of the new compounds described are summarized in Table I.

Details of the work, including the transformation of 2-(2'-hydroxyisopropyl)-7-methoxy-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene (7-methoxyoccidol), (IIIb) to 2-isopropyl-7-methoxy-5,8-dimethyl-1,2,3,

TABLE I

PMR data of new compounds pertaining to the synthetic scheme: VIII → IXa → IXb → IIIb

Compound	m.p.	Solvent	PMR data
7-Methoxy-5,8-dimethyl-3,4-dihydro-2-naphthoic acid VIII	225°	(ethanol)	(CDCl <sub>3</sub> , 60 MHz): 2.34 (6H, s, 2xAr-CH <sub>3</sub> ), 2.66 (4H, m, 2xCH <sub>2</sub> ), 3.87 (3H, s, OCH <sub>3</sub> ), 6.73 (1H, s, H <sub>6</sub> ), and 8.0 (1H, s, H <sub>1</sub> ).
7-Methoxy-5,8-dimethyl-1,2,3,4-tetrahydro-2-naphthoic acid IXa	180°	(ethanol)	(CDCl <sub>3</sub> , 60 MHz): 2.13 (3H, s, Ar-CH <sub>3</sub> ), 2.23 (3H, s, Ar-CH <sub>3</sub> ), 2.4-3.0 (7H, m, aliphatic-H), 3.83 (3H, s, OCH <sub>3</sub> ) and 6.3 (1H, s, H <sub>6</sub> ).
Methyl 7-methoxy-5,8-dimethyl-1,2,3,4-tetrahydro-2-naphthoate IXb	63°	(hexane)	(CCl <sub>4</sub> , 60 MHz): 2.05 (3H, s, Ar-CH <sub>3</sub> ), 2.15 (3H, s, Ar-CH <sub>3</sub> ), 2.2-2.8 (7H, m, aliphatic-H), 3.67 (3H, s, OCH <sub>3</sub> or CO <sub>2</sub> CH <sub>3</sub> ), 3.73 (3H, s, CO <sub>2</sub> CH <sub>3</sub> or OCH <sub>3</sub> ), and 6.77 (1H, s, H <sub>6</sub> ).
2-(2'-Hydroxyisopropyl)-7-methoxy-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene IIIb	84-85°	(hexane)	(CCl <sub>4</sub> , 60 MHz): 1.26 [6H, s, COH (CH <sub>3</sub> ) <sub>2</sub> ], 2.1 (2H, m, non-benzylic CH <sub>2</sub> ), 2.8 (5H, m, 2xbenzylic CH <sub>2</sub> and CH), 3.75 (3H, s, OCH <sub>3</sub> ) and 6.72 (1H, s, H <sub>6</sub> ).

4-tetrahydronaphthalene (II) which played a key role in the structure elucidation of manicol (I) will be published elsewhere.

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1. Polonsky, J., Varon, Z., Jacquemin, H., Donnelly, D. M. X. and Meegan, M. J., *J. Chem. Soc. Perkin Transactions I*, 1980, p. 2065.
2. Anantha Reddy, P., *Ph.D. Thesis*, Indian Institute of Science, Bangalore, October 1978.
3. Hirose, Y. and Nakatsuka, T., *Bull. Agric. Chem. Soc. Japan*, 1959, 23, 143; Tomita, B., Hirose, Y. and Nakatsuka, T., *Mokuzai Gakkaishi* (English), 1969, p. 76; *Chem. Abst.*, 1969, 71, 88431.
4. Anantha Reddy, P. and Krishna Rao, G. S., *Indian J. Chem.*, 1980, 19B, 753.
5. — and —, *Ibid.*, 1981, 20B, 100.
6. Warriner, R. N., Lee, T. S., Russell, R. A. and Paddon-Row, M. N., *Aust. J. Chem.*, 1978, 31, 1113.

## STUDIES OF SOME NAPHTHOTHIA-AZA COMPOUNDS AS PLANT GROWTH PROMOTERS

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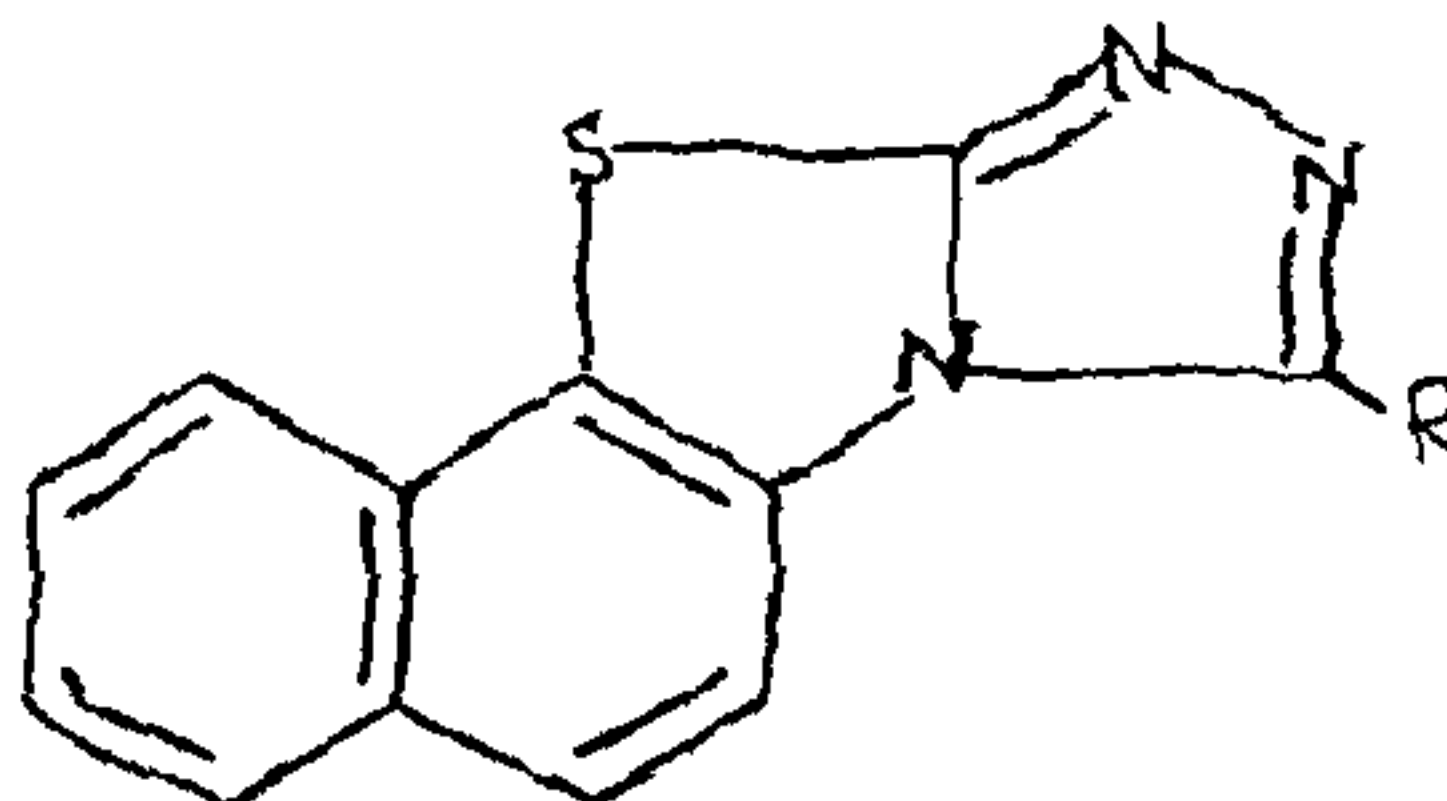
It has been already reported<sup>1,2</sup> that some benzothiazolyl hydrazones are growth promoters in some leguminous plants. Studies are made of some condensed thiazole systems on nodulation by Kulkarni *et al.*<sup>3</sup> and the results were statistically significant. Hence naphthalene system was selected in place of simple benzo-compounds. Hydrazino naphthothiazole<sup>4</sup> was condensed with aldehydes using ethanol as a solvent. The hydrazone was filtered off and recrystallized by DMF. *s*-Triazolo (5, 4-*b*) naphtho (2, 1-*d*) thiazole<sup>5</sup> (I), 3-mercapto-*s*-triazolo (5,4-*b*) naphtho (2, 1-*d*) thiazole (II), 3-hydroxy-*s*-triazolo (5, 4-*b*) naphtho (2, 1-*d*) thiazole (III) and 3-methyl-*s*-triazolo (5,4-*b*) naphtho (2, 1-*d*) thiazole (IV) and the hydrazones selected 5-chloro salicyl (V), *p*-hydroxy phenyl (VI) and phenyl naphthothiazolyl (VII) hydrazones were prepared in this laboratory<sup>6</sup>.

Solution of each compound had a concentration of (5 ppm). Gibberellic acid (GA<sub>3</sub>) was used as

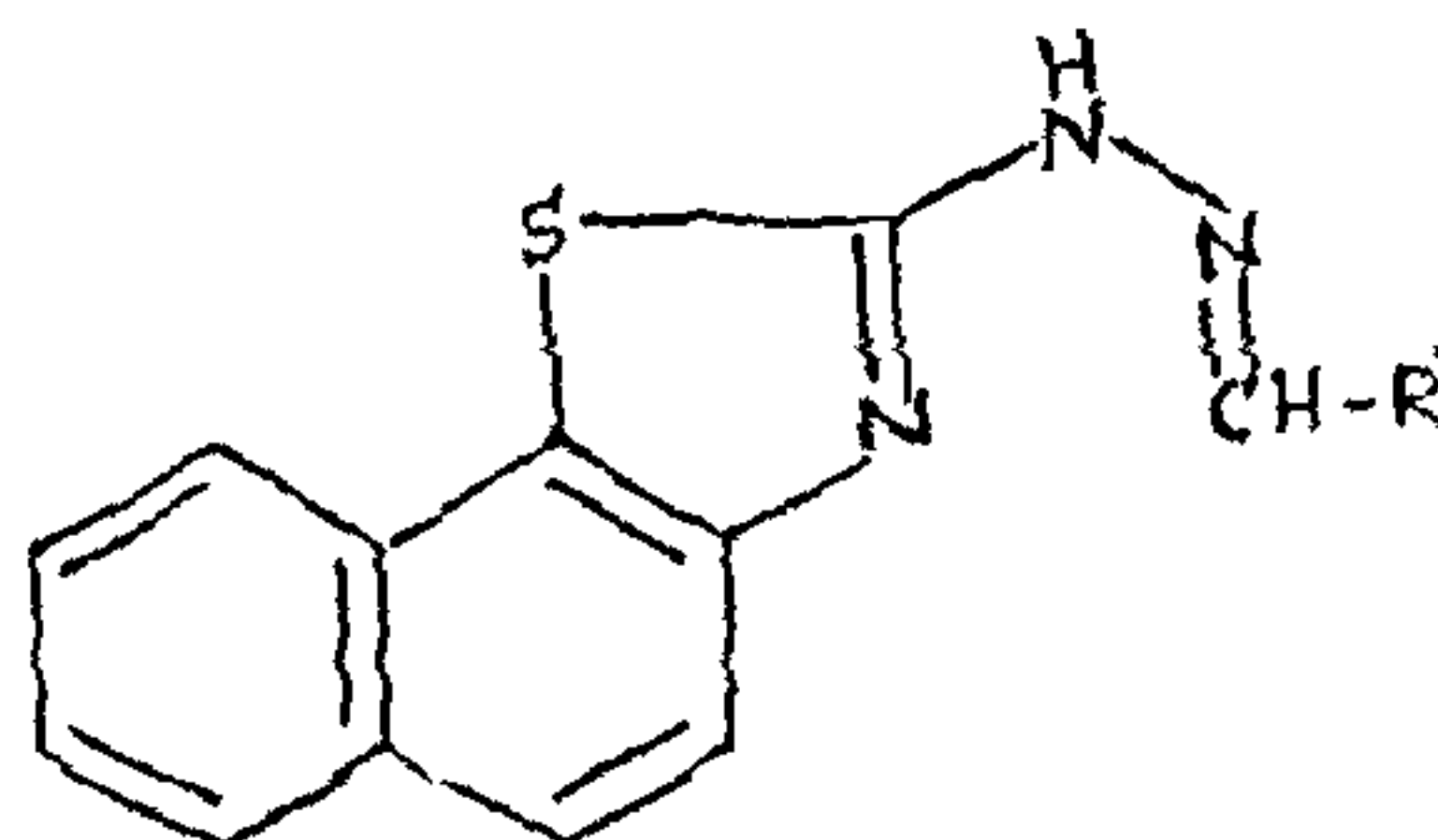
standard and sterile water was kept as control. *Cicer arietinum* was selected as the leguminous plant. Blotters were sterilized at 15 psi for 20 min before use. The experiment was set up in duplicate, 10 seeds in every petridish. Root and shoot lengths were determined. On third day 5 seeds along with root and shoot were dried at  $60 \pm 2^\circ \text{C}$  (Table I). Root and shoot parts were separated, crushed in water and the extract was filtered (15 ml). From this solution amino acids were identified using butanol : acetic acid : water (4 : 1 : 5). The amount of nitrogen was estimated by Kjeldahl's method. Trichloroacetic acid<sup>7</sup> was used for the separation of protein part from non-protein part.

Table I includes the root and shoot length, the percentage difference, amount of nitrogen before and after trichloroacetic acid treatment, the weight of residue from trichloroacetic acid treatment respectively.

Present investigation strengthens our view that the B<sub>2</sub> nucleus, when replaced by polynuclear hydrocarbon, helps in the plant growth activity. It is not only the methyl electron donating group<sup>8</sup> at B<sub>2</sub> that increases the length and dry matter but also the naphthalene ring attached to thiazole system.



*s*-Triazolo (5,4-*b*) Naphtho (2,1-*d*) Thiazoles  
R = —H, —SH, —OH, —CH<sub>3</sub>



Naphthothiazolyl Hydrazones

