TABLE 1

Treatment of Thioacetamide in days and different blood parameters

Time (days)	Erythrocytes count $\times 10^6$/cmm.	Hb%	Leucocytes count $\times 10^3$/cmm.	% of immature erythrocytes	Erythrocytes sedimentation rate
Control	3.95 ± 0.26	14.1 ± 0.7	0.06 ± 0.01	3.9	7.0 ± 1
15	3.80 ± 0.21	13.9 ± 0.8	1.05 ± 0.11	17.0	11.3 ± 1.2
30	3.40 ± 0.19	13.3 ± 0.9	1.16 ± 0.11	26.3	14.5 ± 1
45	2.35 ± 0.23	12.1 ± 0.3	2.35 ± 0.16	65.2	18.0 ± 2

cytes in haemopoetic tissues thereby creating leukaemogenic conditions.

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1. Fitzhugh, O. G. and Nelson, A. A., *Science*, 1948, **108**, 626.
2. Napalkov, N. P., In *Potential carcinogenic hazards from drugs*, (ed. R. Truhaut), Springer-Verlag, Berlin, 1967, 178.
3. Ulland, B. M., Weisburger, J. H., Weisburger, E. K., Rice, J. and Cypher, R., *J. Natl. Cancer Inst.*, 1972, **49**, 583.

SYNTHESIS OF QUEEN BEE PHEROMONE

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THE mandibular glands of the queen honey-bee, *Apis mellifera*, secrete the queen substance which principally contains 9-oxo-Δ^2-decenoic acid. The queen substance inhibits the development of ovaries and prevents queen rearing in workers. It also acts as sex attractant in mating[1].

9-oxo-Δ^2-decenoic acid (VI) has been synthesised from a number of starting materials[2-10]. We report here its synthesis from 7-hydroxyheptanal, one of the periodate oxidation products of aleuritic acid, the major constituent acid of shellac.

7-Hydroxyheptanal (II), on condensation with malonic acid in the presence of pyridine gave an α, β-unsaturated hydroxy acid (III), which on oxidation with pyridiniumchlorochromate resulted in an unsaturated aldehydic acid (IV).

The carbinol (V) obtained by the condensation of IV with CH_3MgI on further oxidation with aluminium tert. butoxide yielded 9-oxo-Δ^2-decenoic acid (VI).

$HOH_2C.(CH_2)_5.CH(OH).CH(OH).(CH_2)_7.CO_2H$ (I)
$HOH_2C.(CH_2)_5.CHO$ (II)
$HOH_2C.(CH_2)_5.CH=CH.CO_2H$ (III)
$OHC.(CH_2)_5.CH=CH.CO_2H$ (IV)
$H_3C.CHOH.(CH_2)_5.CH=CH.CO_2H$ (V)
$H_3C.C.(CH_2)_5.CH=CH.CO_2H$ (VI)

7-Hydroxyheptanal (II)

Threo-aleuritic acid (I, m.p. 99-100°, 8 g) in methanol-water (400 ml, 1:1) at 40° C on sodium periodate oxidation[11] for 10 min and on usual workup afforded 7-hydroxyheptanal as liquid (3.2 g). It was purified through a column of neutral alumina by eluting with ether. I.R.(Neat):3250, 1720 cm^{-1} (Found:C, 64.80; H, 10.72. Calcd. for:$C_7H_{14}O_2$:C, 64.70; H, 10.80%).

9-*Hydroxy*-Δ^2-*nonenoic acid* (III)

The above hydroxyaldehyde (II, 3 g) was heated on a steam bath for 4 hr with malonic acid (3 g) in dry pyridine (5 ml). Extraction with ether yielded the unsaturated hydroxy acid as thick liquid (2.8 g), which was purified over a column of neutral alumina in ether. I.R.(Neat):3250, 1700, 970 cm^{-1} (Found:C, 62.72; H, 9.24. Calcd. for $C_9H_{16}O_3$:C, 62.80; H, 9.30%).

Δ^2-*Noneldehydic acid* (IV)

A solution of III (2 g) in dry methylene chloride (10 ml) was added with stirring to a suspension of pyridinium chlorochromate (3.28 g) and anhy. sodium acetate (0.25 g) in dry methylene chloride. After 2 hr, dry ether was added and the supernatant decanted from the black gummy mass. The ethereal extract was then passed through a column of neutral alumina to remove the impurities and the solvent was

evaporated off to obtain IV (1.4 g) as thick oil. I.R.(Neat): 1725, 1700, 970 cm^{-1} (Found: C, 63.50; H, 8.20. $C_9H_{14}O_3$ requires C, 63.52; H, 8.23%).

9-Hydroxy-Δ^2-decenoic acid (V)[12]

The above compound (IV, 2.5 g) in dry ether (10 ml) was condensed with CH_3MgI. The resultant product (V) obtained as liquid (2 g) was purified through a column of neutral alumina in ether. I.R.(Neat): 3250, 1700, 970 cm^{-1}. (Found: C, 64.42; H, 9.63. $C_{10}H_{18}O_3$ requires C, 64.51; H, 9.70%).

9-oxo-Δ^2-decenoic acid (IV)

The above carbinol (2 g) in a mixture of dry acetone (15 ml) and benzene (20 ml) was heated at 80° for 8 hr with a solution of aluminium tert. butoxide (3.4 g in dry benzene). It was then cooled and treated with 10% H_2SO_4 (10 ml). On workup with benzene, VI was obtained as solid (1.2 g) and was cyrstallised from methanol m.p. 53–55° (lit[7]. 53–54°). The purity of the compound was tested by TLC. I.R.(KBr): 1725, 1700, 970 cm^{-1}. Its 2,4 DNP derivative has m.p. 126–128° (lit[7]. 127–128°) (Found: N, 15.34. Calcd. for $C_{16}H_{20}N_4O_6$: N, 15.40%).

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1. Wigglesworth, V. B., *The principles of insect physiology*, ELBS and Chapman and Hall, London, 1972, 609.
2. Kennedy, J., McCorkindale, N. J. and Raphael, R. A., *J. Chem. Soc.*, 1961, **3**, 3813.
3. Sisido, K., Kawanisi, M., Kondo, K., Morimoto, T., Saito, A. and Hukue, N., *J. Org. Chem.*, 1962, **27**, 4073.
4. Barbier, M. and Lederer, L., *Compt. rend*, 1960, **251**, 1135.
5. Eitler, K., *Ann.*, 1962, **658**, 91.
6. Jaeger, R. H. and Robinson, R., *Tetrahedron*, 1961, **14**, 320.
7. Vig, O. P., Vig, A. K., Grewal, M. S. and Gupta, K. C., *J. Indian Chem. Soc.*, 1975, **52**, 543.
8. Tsuji, J., Masaoka, K. and Takhasi, T., *Tetrahedron Lett.*, 1977, 2267.
9. Subramaniam, C. S., Thomas, P. J., Mamdapur, V. R. and Chadha, M. S., *Indian J. Chem.*, 1978, **16B**, 318.
10. Dzhemilev, U. M., Balezina, G. G. and Tolstikov, G. A., *Chem. Abstr.*, 1980, **93**, 185693 q.
11. Reuter, James M. and Solomon, Robert G., *J. Org. Chem.*, 1978, **43**, 4247.
12. Butler, C. G., Callow, R. K. and Chapman, J. R., *Nature.*, 1964, **201**, 733.

RESPONSE OF CYANOBACTERIAL NITROGEN FIXATION TO INSECTICIDES

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AGROCHEMICALS such as herbicides, fungicides and insecticides are either stimulatory or inhibitory or neutral to cyanobacterial growth and nitrogen fixation[1]. A greater understanding of the impact of a wide range of these chemicals is necessary to appreciate their environmental bearing on the ecology of these organisms, particularly under improved soil and crop management svstems.

The present communication deals with the effect of BHC (γ-1,2,3,4,5,6-hexachlorocyclohexane), Carbofuran (2,3-dihydro 2,2-dimethyl-7-benzofuranyl methyl carbamate) and Phorate (O,O-diethyl-S-ethyl thiomethyl diphosphate) on the chlorophyll *a* synthesis and nitrogen fixation in five cyanobacterial forms, two of which belonging to *Hapalosiphon* (*H. fontinalis* ARM 363, *H. welwitschii* var. *vaginatus* ARM 364), two to *Westiellopsis* (*W. prolifica* ARM 365 and ARM 366) and one to *Calothrix* (*C. braunii* ARM 367). The recommended field doses of these insecticides are 1.5 ppm for BHC, 0.5 ppm for carbofuran and 1 ppm for phorate.

The algae, originally isolated from saline-alkali soils[2] were grown in nitrogen free Fogg's medium[3], supplemented with A_5 solution[4]. The cultures were incubated at 30° C under 2000 lux. The nitrogenase (N-ase) activity was measured in terms of acetylene reduction[5,6] using a Nucon Model GLC 5500 with a Porapak R column. Acetylene, equal to 10% of the total volume was injected and the vials were incubated for 90 min at 30° C under 2000 lux. The reaction was terminated by injecting 0.1 ml TCA (50%) and the gas phase was analysed for ethylene.

For examining the effects of insecticides, 2 ml of algal suspension from an exponentially growing culture were inoculated into 100 ml flasks containing 25 ml Fogg's nitrogen free medium. The pesticides were added to give a final concentration of 1, 10 and 100 ppm. Chlorophyll *a* (Chl *a*) synthesis was measured spectrophotometrically at the end of 14 days' growth in terms of the absorption of methanol (90%) extract.