

INVESTIGATIONS ON THE OFFENSIVE ODOUR OF HEMIPTRA-BUGS

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Black Hemiptera Bugs (Fam: Pentatomidea; Hindi: Tehlen)

generally observed immediately after the rainy season, especially in the tropical regions of the country, whenever disturbed or crushed give off a characteristic nauseating smell.

The compound due to which the bugs possess this obnoxious smell has been obtained in the form of a colourless oil. Its structure has been assigned on the basis of I.R. studies and its synthesis.

Bugs (24 g.), collected soon after their death, were successively extracted in a Soxhlet extractor with petroleum ether (40-60°) for 28 hrs. Most of the solvent from the extract was removed by distillation under reduced pressure and the remainder extract (ca 15 ml.) was shaken well with aq. methanol (1:1 v/v). The petroleum ether layer containing the fatty matter was thus separated from the aq. methanolic

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layer containing the compound, which was purified by direct distillation as a colourless oil (0.9 g.), b.p. 112-113°.

Micro quantities of the oil when subjected to qualitative tests failed to respond for N, S or halogens. 0.4 g. of the oil when dissolved in methanol and treated with methanolic solution of 2,4-dinitrophenylhydrazine immediately resulted in an orange ppt. indicating the presence of a carbonyl group.

This Hydrazone was found to be homogeneous on thin layer chromatography (Silica Gel G, activated at 110° for 24 hrs.) using benzene:ethanol (1:1 v/v, purified before use by standard methods).

That this oil possesses an aldehydic group is exhibited by its positive test for Tollen's reagent and Fehling's soln. and also by its I.R. studies which shows peaks (1) at  $975\text{ cm}^{-1}$  (trans-C=C-),  $1380\text{ cm}^{-1}$  (-C-Me), and at  $1725\text{ cm}^{-1}$  (-CHO). On the basis of these studies and the microanalysis report the structure of the aldehyde has been assigned as trans-4-hepten-1-al;  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CHO}$ . (Found: C, 75.02; H, 10.62; Mol.wt.(Rast), 114. Calc. for  $\text{C}_7\text{H}_{12}\text{O}$ : C, 75.00; H, 10.71% Mol.wt. 112.)

Its 2,4-dinitrophenylhydrazone obtained as described above was crystallised from ethanol in dull orange needles (1 g.) m.p. 120°. (Found: C, 53.33; H, 3.96; N, 19.02. Mol.wt.(Rast), 290. Calc. for  $\text{C}_{13}\text{H}_{16}\text{O}_4\text{N}_4$ : C, 53.42; H, 4.10; N, 19.17%. Mol.wt. 292).

Its structure was further confirmed by comparing its I.R. spectrogram with that of the synthetic sample obtained by the

method already reported(2). Thus pent-1-en-3-ol, obtained by treating vinyl magnesium bromide with propionaldehyde was converted into its vinyl ether(3) by mercuric acetate catalysed trans-etherification with ethyl vinyl ether. The vinyl ether thus obtained when subjected to the Claisen rearrangement(4) furnished trans-4-hepten-1-al(2) in 70% yield. b.p. 112-113°. (Found: C, 74.92; H, 10.55. Calc. for  $C_7H_{12}O$ : C, 75.00, H, 10.71%.)

The 2,4-dinitrophenylhydrazone was crystallised from ethanol in dull orange needles m.p. 120°. (Found: C, 53.39; H, 3.99; N, 19.01. Calc. for  $C_{13}H_{16}O_4N_4$ : C, 53.42; H, 4.10; N, 19.17%.) (Mixed m.p. of both the samples remains undepressed).

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