530. *The Odoriferous Secretion of the Water Bug,* Sigara falleni *(Fieb.)*

By A. R. Pinder and B. W. Staddon

The main constituent of the odoriferous secretion of *Sigara falleni* (Fieb.) is *trans*-4-oxohex-2-enal (*trans*-3-propionylacraldehyde). An unidentified minor component is also present.

Integumentary glands which produce odoriferous substances are of widespread occurrence in the insect order Heteroptera (bugs).[1] Paired dorso-abdominal glands are present in the nymphs, but at the adult moult they are replaced by glands in the metathorax which open to the exterior on the ventral surface. Short-chain (C_6—C_{10}) saturated and $\alpha\beta$-unsaturated aldehydes have been found in the secretions of coreid [2,3] and pentatomid [3-10] bugs, and in that of the bed bug, *Cimex lectularius* L.,[10] while dodecane, tridecane,[3-5,7,9] unidentified dicarbonyl compounds,[3,4,7,9] furans, quinones,[11] and *trans*-hex-2-enyl acetate [12,13] have been found in similar sources.

The secretion of the aquatic bug, *Sigara falleni* (Fieb.), is a pale yellow oil with an odour reminiscent of " leaf aldehyde " (hex-2-enal), but somewhat more pungent. Gas chromatography showed that before purification it was substantially a single product, but contained a more volatile impurity (<5%), with a retention time about half that of the major component, which was largely eliminated by distillation *in vacuo*. Analysis revealed a formula $C_6H_8O_2$, confirmed by mass spectrometry. The chemical properties were those of an aldehyde (reduction of Tollens's reagent and of Fehling's solution, and formation of a reddish-purple colour with Schiff's reagent); $\lambda_{max.}$ (methanol) 215 mμ, $\nu_{max.}$ 2840, 2740 (aldehyde C–H), 1690 ($\alpha\beta$-unsaturated C=O), 1621 (conjugated C=O), and 980 cm.$^{-1}$ (*trans* CH=CH). It formed a bis-2,4-dinitrophenylhydrazone which gave the characteristic deep blue colour with alcoholic potassium hydroxide,[14] and had an ultraviolet absorption curve, similar to that of such derivatives of conjugated diketones containing the grouping $O=\overset{|}{C}-C=C-\overset{|}{C}=O$,[15] which was superimposable upon the curve for β-acetylacraldehyde (I; R = Me) bis-2,4-dinitrophenylhydrazone.[16a] It appeared, therefore, that the natural

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[1] R. Poisson, *Traité de Zoologie*, 1951, **10**, 1657.

[2] M. S. Blum, R. D. Crain, and J. B. Chidester, *Nature*, 1961, **189**, 245.

[3] D. F. Waterhouse, D. A. Forss, and R. H. Hackman, *J. Insect. Physiol.*, 1961, **6**, 113.

[4] M. S. Blum and J. G. Traynham, Proc. XIth Internat. Congress Entomol., Vienna, 1960, **3**, 48 (Symposia 3 and 4).

[5] M. S. Blum, J. G. Traynham, J. B. Chidester, and J. D. Boggus, *Science*, 1960, **132**, 1480.

[6] M. S. Blum, *Ann. Entomol. Soc. Amer.*, 1961, **54**, 410.

[7] R. J. Park and M. D. Sutherland, *Austral. J. Chem.*, 1962, **15**, 172.

[8] H. Schildknecht, K. H. Weis, and H. Vetter, *Z. Naturforsch.*, 1962, **17*b***, 350.

[9] H. T. Gordon, D. F. Waterhouse, and A. R. Gilby, *Nature*, 1963, **197**, 818.

[10] H. Schildknecht, *Angew. Chem. Internat. Edn.*, 1964, **3**, 73.

[11] J. D. Loconti and L. M. Roth, *Ann. Entomol. Soc. Amer.*, 1953, **46**, 281.

[12] A. Butenandt, *Nova Acta Leopoldina*, 1955, **17**, 445 (*Chem. Abs.*, 1957, **51**, 7595).

[13] A. Butenandt and N.-D. Tâm, *Z. physiol. Chem.*, 1957, **308**, 277.

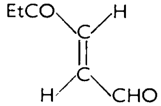
[14] H. H. Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 758.

[15] Cf. K. G. Lewis, *J.*, 1956, 1083.

[16] Cf. (*a*) L. Birkofer and R. Dutz, *Annalen*, 1962, **657**, 94; (*b*) J. Levisalles, *Bull. Soc. chim. France*, 1957, 997; (*c*) J. Šrogl, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1380.

product was a β-acylacraldehyde; the single carbonyl band in its infrared spectrum, even under high resolution, seemed to refute this, but the fact that β-acetylacraldehyde has but a single carbonyl band,[16a] at 1692 cm.$^{-1}$, supported the view. Taking into account the

R·CO·CH=CH·CHO
(I)

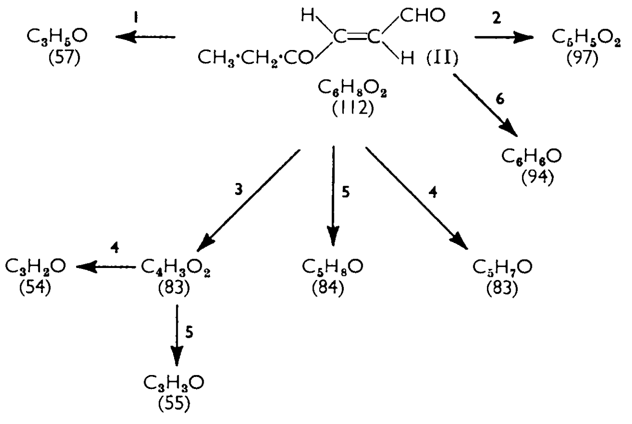


(II)

molecular formula and chemical properties, we formulate the product as β-propionylacraldehyde (I; R = Et), which, on infrared evidence (see above), must have the *trans*-configuration (II).

Mass spectrometry results are in reasonable agreement with this formulation, the observed peaks being explained as shown (*m/e* values in parentheses). High resolution showed the peak at *m/e* 83 to be a doublet of approximately equal intensities, corresponding to the fragments $C_4H_3O_2$ and C_5H_7O. A peak at *m/e* 69, corresponding to C_4H_5O (III), is an unusual feature of the spectrum; it must be explained by cleavage of the ethylenic bond in (II), an unexpected fracture on the basis of experience with singly-conjugated olefinic bonds:[17]

A synthesis of *trans*-β-propionylacraldehyde (II) was effected, starting with furan. Successive acetylation and Wolff–Kishner reduction afforded 2-ethylfuran (IV), which with bromine and methanol gave 2-ethyl-2,5-dihydro-2,5-dimethoxyfuran (V). This was not isolated, since it underwent spontaneous acid-catalysed cleavage to *trans*-β-propionylacraldehyde (II). The ultraviolet and infrared spectra of the product were very nearly identical with those of the natural product, but gas chromatography showed that it was



1, −CH=CH·CHO; 2, −Me; 3, −Et; 4, −CHO; 5, −CO; 6, $-H_2O$

a mixture, with (II) as major component. The formation of several products by such cleavage of dihydrofurans of type (V) has been reported.[16c] The crude product yielded a 2,4-dinitrophenylhydrazone identical with that of the natural product. The immediate cleavage product of (V) would be the *cis*-isomer of (II), which would be expected to be isomerised readily to the more stable *trans*-isomer under the ring-cleavage conditions.[16b]

Weak hydroxyl absorption was noted in the infrared spectrum of the natural product. We suggest that this is due to the presence of the hydrate of (II), which would be expected

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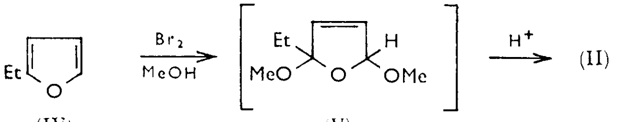
[17] See, *e.g.*, K. Biemann, " Mass Spectrometry," McGraw-Hill, New York, 1962, ch. 3.

to form a hydrate (VI) because of the relay to the aldehyde group, through the conjugated system, of the electron-attracting influence of the ketonic carbonyl group. The formation of a hydrate by β-acetylacraldehyde has been reported.[16a]



(IV) (V)

EtCO·CH = CH·CH(OH)$_2$

(VI)

It is apparent from the position of the ultraviolet absorption maximum in methanol (215 mμ) that in this solvent the natural product is present as its hemiacetal, the absorption being that of a conjugated enone.

[*Added December 29th* 1964. After this Paper had been accepted for publication, the isolation of *trans*-4-oxohex-2-enol from the Australian green vegetable bug, *Nezara viridula* L., was reported (A. R. Gilby and D. F. Waterhouse, *Austral. J. Chem.*, 1964, **17**, 1311).]

EXPERIMENTAL

Gas chromatography was effected on a Pye Argon Chromatograph. Infrared spectra were measured on Perkin-Elmer Infracord 237 and Unicam S.P. 100 instruments, and ultraviolet spectra on a Unicam S.P. 700 instrument.

Isolation of Bug Secretion.—Adult specimens of *S. falleni* were collected from Llangorse Lake, near Brecon, during March and April 1964. Each specimen was narcotised with carbon dioxide and secured, ventral side uppermost, on the stage of a dissecting microscope. The cuticle surrounding the external opening of the reservoir was detached and the latter drawn out and air-dried. The contents of the reservoir were sucked out using a capillary pipette. The yield from 100 insects (3—5 mg.) was dissolved in ether and the solution dried (Na_2SO_4). Evaporation of the solvent left a yellow oil b. p. 95—100° (bath)/11 mm., which gas chromatography (20% Apiezon L on 100—120 mesh Celite at 105°) showed to be substantially a single species, but a small peak with a retention time about half that of the main peak indicated the presence (*ca.* 3%) of a more volatile impurity. A further distillation virtually eliminated this, yielding a yellow *oil* with a pleasant, yet somewhat pungent, odour (Found: C, 63·9; H, 7·2. $C_6H_8O_2$ requires C, 64·3; H, 7·2%). The molecular formula and molecular wt. (parent-ion peak at mass 112) were confirmed by mass spectrometry; $\lambda_{max.}$ (MeOH) 215 mμ (ε 7350); $\nu_{max.}$ (film) 2840, 2740, 1690, 1621, and 980 cm.$^{-1}$. Weak hydroxyl absorption at 3500 and 1120 cm.$^{-1}$ (aldehyde hydrate?) was also observed. Mass spectrum: peaks at *m*/*e* 112, 97, 94, 84, 83, 69, 57, 55, and 54.

The product reduced Tollens's reagent in the cold, and Fehling's solution, and gave a reddish-purple colour with Schiff's reagent. A *bis*-2,4-*dinitrophenylhydrazone*, prepared in ethanol–sulphuric acid, formed dark red prisms, m. p. 247—248° (decomp.) (from dimethylformamide) (Found: C, 46·3; H, 3·4; N, 23·6. $C_{18}H_{16}N_8O_8$ requires C, 45·8; H, 3·4; N, 23·7%); $\lambda_{max.}$ ($CHCl_3$) 400—500 mμ (broad, intense band), with ill-defined maxima at 435 (ε 41,300) and 478 mμ (ε 38,350).[15] The derivative gave a deep blue colour with alcoholic potassium hydroxide.[14]

2-*Acetylfuran.*—The ketone was prepared by acetylation of furan,[18] and by reaction of 2-cyanofuran [19] with methylmagnesium iodide.[20] It distilled at 71—72°/16 mm., 73—74°/18 mm.

2-*Ethylfuran.*—Wolff–Kishner reduction [21] of 2-acetylfuran was best effected through the semicarbazone, m. p. 149—150° (lit.,[22] 148°). This derivative (40 g.) and finely-powdered potassium hydroxide (60 g.) were mixed intimately and heated gently, with a free flame, until decomposition was complete. The vapours were condensed and the condensate mixed with ether and saturated sodium hydrogen sulphite solution, and shaken. The ether layer was washed with water, dried, and evaporated, leaving 2-ethylfuran, which was distilled through a short Vigreux column, b. p. 92—93° (8·5 g.) (lit.,[21] 92—95°).

[18] H. D. Hartough and A. I. Kosak, *J. Amer. Chem. Soc.*, 1946, **68**, 2639.
[19] A. Pinner, *Ber.*, 1892, **25**, 1414.
[20] Y. Asahina and Y. Murayama, *Arch. Pharm.*, 1914, **252**, 435.
[21] A. K. Armitage and H. R. Ing, *Brit. J. Pharmacol.*, 1954, **9**, 376.
[22] L. Bouveault, *Ber.*, 1901, **34**, 1072.

Reaction of 2-Ethylfuran with Bromine and Methanol.[16]—(*a*) 2-Ethylfuran (6·5 g.), methanol (250 c.c.), dry ether (50 c.c.), and powdered anhydrous sodium carbonate (30 g.) were stirred and cooled to −5°. A cooled solution of bromine (10·2 g.) in methanol (150 c.c.) was added during 30 min. at −5°, with stirring. After a further 1½ hr. at 0° the mixture was poured into saturated aqueous sodium chloride (400 c.c.) and extracted several times with ether. The dried (Na_2SO_4) extract was concentrated *via* a column, leaving a liquid, b. p. 88—89°/17 mm. (2·5 g.), with much high-boiling residue. The distillate had an odour resembling closely that of the insect secretion, and showed the same reducing properties. The ultraviolet and infrared spectra were almost identical within those of the natural product, but gas chromatography of the synthetic material showed the presence of two major products, one of which had a retention time identical with that of the natural product. The synthetic product formed a bis-2,4-dinitrophenylhydrazone, which formed dark red prisms, m. p. 247—248° (decomp.) (from dimethylformamide) (Found: C, 46·1; H, 3·3; N, 23·5%). Mixed m. p.s with the corresponding derivative of the natural product, and ultraviolet and infrared spectra were identical.

(*b*) 2-Ethylfuran (8·2 g.), methanol (100 c.c.), and powdered anhydrous potassium acetate (25 g.) were stirred at −40° during the dropwise addition (30 min.) of a cooled (−30°) solution of bromine (15 g.) in methanol (100 c.c.). The mixture was stirred for 8 hr. at room temperature, poured into saturated aqueous sodium chloride (250 c.c.), and rendered alkaline with solid sodium carbonate. The product, isolated with ether and distilled at 91—92°/19 mm. (3·0 g.), was identical (spectral comparison) with that obtained under (*a*).

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DEPARTMENTS OF CHEMISTRY AND ZOOLOGY, UNIVERSITY COLLEGE, CARDIFF.
[Present address (A. R. P.): THE FLORIDA STATE UNIVERSITY,
TALLAHASSEE, FLORIDA, U.S.A.]

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