afforded the corresponding ester (V) along with a small quantity of an unidentified compound m.p. 121°. All the compounds gave expected C, H analysis and IR-and NMR-spectra. The ester (V) on reduction with lithium aluminium hydride afforded the corresponding primary alcohol (VI) which on oxidation with manganese dioxide afforded the aldehyde (VII, semicarbazone m.p. 167°). This aldehyde on Wolff Kishner reduction afforded a quantitative yield of 1,6-dimethyl-4-ethyl naphthalene (III m.p. and mixture m.p. with the TNB complex of an authentic sample of III, 135°).

It is interesting to note that when the acid (IV) was subjected to dehydrogenation with selenium at 280° most of it invariably escaped and was deposited on the cooler surface of the apparatus. The reacted material after 20 h

was again found to be the same mixture of the two naphthalenes (II and III). The acid (IV) thus represents the second example where a carboxyl group is reduced to a methyl during selenium dehydrogenation.

Zusammenfassung. Neue Befunde zur Interpretation der Selendehydrierung.

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Biological Activity of Synthetic Moulting Hormone Analogues in the Blowfly Calliphora stygia

An early study¹ of the biological activity of synthetic ecdysone analogues with fewer hydroxy groups than α -ecdysone (I) indicated that such compounds are of greatly reduced biological activity. However, our observation² that the 2-deoxy compounds (II) and (III) are as active in the *Calliphora* bioassay as β -ecdysone (IV) has led us to examine the activities of other less hydroxylated 2-deoxyecdysone analogues for comparison with those of several 2-hydroxy analogues. It was found that 2, 22, 25-trideoxy- α -ecdysone (V)³ showed remarkably high activity (see Table). Even the simple ketol (VI)³ showed a response, though much weaker. The 5α -analogues of these compounds were inactive. Surprisingly 22, 25-dideoxy- α -ecdysone (VII)⁴ is less active than (V) indicating

 \mathbb{R}^1 \mathbb{R}^2 \mathbb{R}^3 R4 R^5 OH OHΗ OH OH(I)OHOHOH (II)Η H (III)Н OHOHOH OH(IV) OH OH OHOH OH (V)Н OHH Η Η (VI) H H Η Н Η (VII) OHOHΗ Η OHOHН OH(VIII) Н (IX) OH OH Н OH H

Biological activity in the Calliphora bioassay of ecdysone analogues compared with $\beta\text{-ecdysone}$

Compound a	Concentration (%) required to produce 60-70% response	Relative activity
(IV) β -ecdysone	0.001	1
(V) 2,22,25-trideoxy-α-ecdysone	0.003	1/3
(VI) 2,14,22,25-tetradeoxy- α-ecdysone	0.1	1/100
(VII) 22,25-dideoxy-α-ecdysone	0.01	1/10
(VIII) 22-deoxy-α-ecdysone	0.02	1/20
(IX) 25-deoxy-α-ecdysone	0.01	1/10

 $[^]aAdministered$ as a 3 μl dose of aqueous solution containing Tween 80 (5%) and ethanol (5%).

that the presence of the 2-hydroxy group actually reduces the activity. The analogues (VIII) 5 and (IX) 5 with additional side-chain hydroxyls were also less active than (V).

$$R^{1}$$
 R^{2}
 R^{2}
 R^{3}
 R^{4}
 R^{5}

The high activity of (V) could be due to its effectiveness as a moulting hormone per se or, perhaps more likely, to its more efficient metabolism to β -ecdysone in the test abdomens than 2-hydroxy analogues. It is thus likely that biosynthesis of β -ecdysone in *Calliphora* proceeds through 2-deoxy intermediates at the early stages of the pathway 6 .

 $\it R\'esum\'e$. L'activité biologique de la 2, 22, 25-trideoxya-ecdysone chez $\it Calliphora$ est plus élevée que celle de toutes les substances analogues examinées.

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- ³ Prepared from the 5α-epimer by base catalyzed equilibration and separation of the epimers produced by alumina chromatography.
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