C 56.97, H 5.90, mol. wt. 990.9; Found: C 57.07, H 6.06, mol. wt. 976.2 (vapor pressure osmometry in $CHCl_3$), the NMR-spectrum ($CDCl_3$) showed signals attributable to 3 aromatic methoxyls at δ 3.80(s), 3.85(s), seven aliphatic acetyls at δ 1.90(s), 2.05(s) and an anomer at δ 4.55 (d, J = 6 cps, β-linkage). Hydrolysis of I with 10% H_2SO_4 solution or emulsion gave D-glucose, which was detected by paper chromatography and gas-liquid chromatography as trimethylsilyl ether, and arctigenin, mp 94–95°, which was identified with an authentic sample by mixed melting point, mass and infrared spectral comparisons.

The permethyl ether prepared by the methylation of I with NaH, DMSO and CH_3I (HAKOMORI's method[5]) afforded on methanolysis with 3% methanolic hydrogen chloride methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside and methyl 2,3,4-tri-*O*-methyl-D-glucopyranoside in almost equal ratio to those prepared from permethyl gentiobiose[6], which were detected by gas-liquid chromatography: condition: column temperature, 175°; carrier gas: N_2 (30 ml/min). On JEOL-JGC 1100 with flame ionization detector.

Therefore, the structure of I has been established to be 4′-*O*-(6-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl) arctigenin (arctigenin-4′-β-gentiobioside).

Zusammenfassung. Eine neue Lignansubstanz, Arctigenin-4′-β-gentiobiosid $C_{33}H_{44}O_{16}\cdot H_2O$ wurde als weisses Pulver von Smp. 174–176° aus Stengeln von *Trachelospermum asiaticum* Nakai var. *intermedium* Nakai gewonnen.

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[6] We are grateful to Dr. S. KIKUMOTO for permethyl gentiobiose.

Dehydrogenation of Khusilic Acid

In an earlier communication[1] a rare reduction of the carboxyl group of khusilic acid (I) to a methyl during selenium dehydrogenation to afford 1,6-dimethyl-4-ethyl naphthalene (III) in addition to the expected product 1, methyl 4-ethyl naphthalene (II) was described. In order to throw more light on this unusual reduction during dehydrogenation, we studied the dehydrogenation of khusilic acid under various other conditions and the results are incorporated in the present communication.

Khusilic acid (I) upon dehydrogenation with Pd-C (30%) in an atmosphere of carbondioxide at 280° for 20 h leads to the formation of only one naphthalene on the basis of TLC (silica gel G plates impregnated with trinitrobenzene) identified as (II). Even after vigorous conditions of this dehydrogenation not even a trace of (III) was formed. This observation is in complete accord with the literature[2], since the reduction of a carboxyl group to a methyl has been only observed during dehydrogenation using selenium.

When the dehydrogenation of khusilic acid was carried out with equal quantity of Pd-C 30% at 280° for 15 min, it afforded a crystalline acid ($C_{14}H_{14}O_2$ m.p. 185°) in quantitative yields. The IR-spectrum of the acid showed intense bands at 3050 (bonded OH of a carboxyl group), 1680 (Ar-COOH) and at 1615, 1585, 1510, 832 and 752 cm^{-1} (aromatic ring).

The NMR-spectrum of the acid displayed a triplet at 1.42 δ (J = 7 Hz, $-CH_2-CH_3$) a quartet at 3.2 δ (J = 7 Hz, $-CH_2-CH_3$) a singlet at 2.71 δ (Ar $-CH_3$) a singlet at 7.3 δ (C_2 and C_3 protons) a broadened singlet at 8.1 δ (C_7 and C_8 protons) a broadened singlet due to meta coupling at 8.7 δ (C_5 H) and a broad signal at 10.93 δ ($-COOH$). This spectroscopic data suggested structure (IV) for this compound which has also been confirmed chemically. The acid (IV) on reaction with diazomethane

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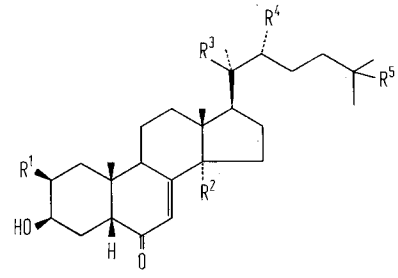
Biological Activity of Synthetic Moulting Hormone Analogues in the Blowfly *Calliphora stygia*

An early study[1] 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 observation[2] 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 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^3	R^4	R^5
(I)	OH	OH	H	OH	OH
(II)	H	OH	H	OH	OH
(III)	H	OH	OH	OH	OH
(IV)	OH	OH	OH	OH	OH
(V)	H	OH	H	H	H
(VI)	H	H	H	H	H
(VII)	OH	OH	H	H	H
(VIII)	OH	OH	H	H	OH
(IX)	OH	OH	H	OH	H

Biological activity in the *Calliphora* bioassay of ecdysone analogues compared with β-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

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

Résumé. L'activité biologique de la 2, 22, 25-trideoxy-α-ecdysone chez *Calliphora* est plus élevée que celle de toutes les substances analogues examinées.

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[4] We thank Dr. P. Hocks, Schering AG, Germany, for this sample.

[5] We thank Dr. J. B. Siddall, Zoecon Corp., California, for these samples.

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