Δ^{16}-Verbindung entsteht. Aus **7** erhielt man durch Oxidation mit Chromsäure das 16-Ketolacton **8**, Smp. 181.5–182.5°, welches durch Bromierung und Dehydrobromierung in das Δ^{14}-16-Keton **9**, Smp. 166.5–167°, übergeführt wurde.

Zur Einführung der 14β-Hydroxygruppe wurde **9** mit $LiAl(t\text{-}BuO)_3H$ zu **10**, Smp. 195–196°, reduziert, der entstandene Allylalkohol **10** mit Peressigsäure zum 14β, 15β-Epoxid **11**, Smp. 200.5–201°, oxidiert und das Epoxylacton **11** mit $LiAlH_4$ zum Pentol **12**, Smp. 220–222°, umgesetzt.

Nach Schutz der beiden Hydroxygruppen an C-14 und C-18 als Acetonid[10] **13**, Acetylierung zu **14** und Acetonidspaltung zu **15**, Smp. 103–105°, wurde durch selektive Oxidation der primären Hydroxygruppe mit DMSO/Pyridin · SO_3[9] das Lactol **16**, Smp. 94–98°, erhalten. Die Umsetzung von **16** mit Methylamin in Aethanol bei 120° ergab das N-Methylaminoepoxid **17**, das mit PtO_2 in Eisessig zum N-Methylaminotriol **18**, hydriert wurde. Nach N-Acylierung von **18** mit Chloracetylchlorid[4] in Tetrahydrofuran zu **19**, Smp. 192–193°, erfolgte die selektive Cyclisation[11] mit Kalium-t-butylat bei −20° zum 3β-Acetoxy-16β, 20β-dihydroxy-4′-methyl-18-nor-5β, 14β-pregnano[13, 14-f]hexahydro-1′, 4′-oxazepin-3′-on (**20a**), NMR-Signale[12]: δ 0.95 (s, 3H, C-19H), 1.35 (d, J = 6Hz, 3H, C-21H), 2.03 (s, 3H, $COCH_3$), 3.05 (s, 3H, N-CH_3), 3.42 und 4.51 (d, d, J = 14Hz, 2H, C-18H), 4.13 (m, W1/2 = 22Hz, 2H, C-16H und C-20H), 4.39 (s, 2H, $COCH_2$), 5.04 (m, W 1/2 = 7Hz, 1H, C-3H); MS: *m/e* 463 [M], 445, 433, 432, 360, 332, 300, 270, 102, 73, 44, 43.

Durch Acetylieren von **20a** in Pyridin mit Acetanhydrid bei 100° erhält man die Verbindung **20b**, Smp. 228–229°, NMR-Signale[12]: δ 0.96 (s, 3H, C-19H), 1.22 (d, J = 6Hz, 3H, C-21H), 2.02, 2.04 und 2.06 (s, s, s, 9H, 3 × $COCH_3$), 2.59 und 4.77 (d, d, J = 14Hz, 2H, C-18H), 2.95 (s, 3H, N-CH_3), 4.28 (s, 2H, $COCH_2$), 5.08 (m, W 1/2 = 15Hz, 3H, C-3H, C-16H und C-20H); MS: *m/e* 547 [M], 517, 516, 488, 487, 458, 457, 428, 427, 360, 332, 327, 300, 267, 266, 102, 101, 73, 44, 43.

Die Cyclisierung zur Hydroxygruppe an C-14 unter Ausbildung des Homomorpholinonderivates **20 a** ergibt sich aus der Acetylierbarkeit der 16β- und 20β-Hydroxygruppen (paramagnetische Verschiebung der Protonen an C-16 und C-20 im NMR um etwa 1 ppm) zu dem Triacetat **20b** und den charakteristischen Fragmentierungen in den Massenspektren von **20a** und **20b**[13].

Summary. The synthesis of 3β-acetoxy-16β, 20β-dihydroxy-4′-methyl-18-nor-5β, 14β-pregnano[13, 14-f]hexahydro-1′, 4′-oxazepin-3′-one (**20a**) is described.

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Forschungsabteilung der F. Hoffmann-La Roche & CO AG,
CH-4002 Basel (Schweiz), 13. April 1971.

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[5] E. Caspi und Y. Shimizu, J. org. Chemistry *30*, 223 (1965).

[6] Die Verbindungen *3* bzw. *7* und *16* sind Stereoisomerengemische an den Zentren C-20 bzw. C-18. Die Substanzen *4* und *5* sind an beiden Zentren epimer. Die Synthesenstufen *3*→*5* wurden ursprünglich parallel mit den reinen 20R- und 20S-Verbindungen durchgeführt. Über die Strukturbeweise wird in einer späteren Mitteilung ausführlich berichtet.

[7] Alle Verbindungen ausser *17* sind analysiert und durch physikalisch chemische Messungen in ihrer Struktur gesichert.

[8] Ch. Meystre, K. Heusler, J. Kalvoda, P. Wieland, G. Anner und A. Wettstein, Helv. chim. Acta *45*, 1317 (1962).

[9] J. R. Parikh und W. von E. Doering, J. Am. chem. Soc. *89*, 5505 (1967).

[10] Diese Reaktion, die von den sechs möglichen Acetoniden mit bemerkenswerter Selektivität nur das gewünschte, propellanartige *13* entstehen lässt, wird in Tetrahydrofuran mit Aceton/BF_3-Aetherat ausgeführt.

[11] Der Aufbau des Homomorpholinonringes erfolgte wie bei Wehrli[4], im Hinblick auf die freien Hydroxygruppen, jedoch unter den angegebenen milden Bedingungen.

[12] Die NMR-Spektren wurden in $CDCl_3$ bei 100 MHz mit TMS als internem Standard aufgenommen.

[13] Herrn Dr. G.-A. Hoyer (Schering AG, Berlin/Bergkamen) sei für die Messungen und Interpretationen der Spektren gedankt.

Dihydropyrrolizine Derivatives in the 'Hair-Pencil' Secretions of Danaid Butterflies

Male butterflies of the family Nymphalidae, subfamily Danainae, possess a pair of extrusible hair-pencils which are used to disseminate pheromonal substances during courtship[1,2]. One substance found in the hair-pencil secretions of the species *Lycorea ceres ceres*, *Danaus gilippus berenice* and *D. gilippus strigosus* and shown to be essential for the mating process in *D. gilippus berenice*[2,3] is the dihydropyrrolizine derivative (I)[4,5]. We have examined the hair-pencil secretions of 6 species of Danainae found in northern Australia. The hair-pencils were removed from live male butterflies and extracted with methylene chloride. 4 species contained dihydropyrrolizines [Table (I)], the compounds identified being the ketone (I) and the related aldehydes (II) and (III).

The dihydropyrrolizines (I) to (III) are structurally similar to the aminoalcohols of the hepatotoxic pyrrolizidine alkaloids[6] and even more closely similar to the dihydropyrrolizine derivatives such as (IV) which are produced metabolically in rats treated with these alkaloids[7]. We have previously prepared the components (I) to (III), and the related alcohols (IV) to (VII), in connection with studies on the liver metabolites of the alkaloids[8].

Thin-layer (TLC) and gas-liquid chromatography of the colourless, semi-crystalline extract (15 mg) from *Danaus hamatus hamatus* (Macl.) (165 males) showed the

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[1] L. P. Brower, J. V. Z. Brower and F. P. Cranston, Zoologica *50*, 1 (1965).

[2] T. E. Pliske and T. Eisner, Science *164*, 1170 (1969).

[3] D. Schneider and U. Seibl, Science *164*, 1173 (1969).

[4] J. M. Meinwald and Y. C. Meinwald, J. Am. chem. Soc. *88*, 1305 (1966).

[5] J. M. Meinwald, Y. C. Meinwald and P. H. Mazzocchi, Science *164*, 1174 (1969).

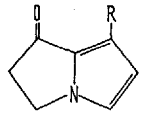
[6] L. B. Bull, C. C. J. Culvenor and A. T. Dick, in *The Pyrrolizidine Alkaloids* (North-Holland Publishing Co., Amsterdam 1968).

[7] M. V. Jago, J. A. Edgar, L. W. Smith and C. C. J. Culvenor, Molec. Pharmac. *6*, 402 (1970).

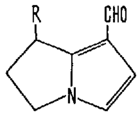
[8] C. C. J. Culvenor, J. A. Edgar, L. W. Smith and H. J. Tweeddale, Aust. J. Chem. *23*, 1853 and 1869 (1970).

presence of 2 main components with the same chromatographic properties and colour reactions with Ehrlich's reagent as authentic samples of the ketone (I) and the hydroxyaldehyde (II). Reduction of the extract with sodium borohydride gave 2 products with Rf and Ehrlich colours identical with those of the alcohols (IV) and (VI). The mass and nuclear magnetic resonance NMR spectra of the hair pencil extract were consistent with the extract being very largely a mixture of the ketone (I) and the hydroxyaldehyde (II) in the ratio of 6:1. The 2 compounds were isolated by preparative TLC and showed the same mass- and NMR-spectra as authentic samples of (I) and (II). The ketone had melting point 74–75° (lit.[4], mp 74–75°) after sublimation.

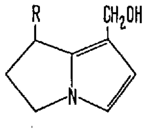
The extract from *Danaus affinis affinis* (Fab.) (15 males) contained 2 main Ehrlich positive components with Rf values and colour reactions identical with authentic samples of (I) and (III). The mass spectrum of the extract was consistent with a mixture of (I) and (III), and sodium borohydride reduction gave the 2 known alcohols (V) and (VI), chromatographically identical with authentic samples.



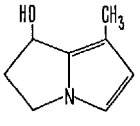
(I) R=CH$_3$
(VII) R-CH$_2$OH



(II) R-OH
(III) R=H

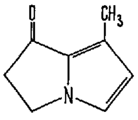
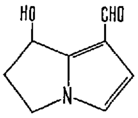
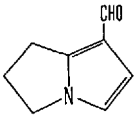


(IV) R-OH
(V) R=H



(VI)

The occurrence of dihydropyrrolizines in butterfly species, subfamily danainae

Butterfly species	 (I)	 (II)	 (III)
Danaus hamatus hamatus (Macl.)	+	+	—
D. affinis affinis (Fab.)	+	—	+
D. plexippus plexippus (L.)	—	—	—
Euploea tulliola tulliola (Fab.)	—	+	—
E. sylvester sylvester (Fab.)	trace ?	+	—
E. core corinna (Macl.)	—	—	—

Euploea tulliola tulliola (Fab.) (1 male) and *E. sylvester sylvester* (Fab.) (2 males) gave extracts which on TLC showed one main Ehrlich positive spot with Rf and colour indistinguishable from an authentic sample of the hydroxyaldehyde (II). Reduction of the extracts with sodium borohydride in each case gave the diol (IV), characterized by its Rf and Ehrlich colour. *E. sylvester sylvester* also contained traces of other Ehrlich positive substances, one with the same chromatographic properties as the ketone (I) but confirmation of this and actual isolation of the hydroxyaldehyde (II) from *E. tulliola tulliola* and *E. sylvester sylvester* awaits the collection of further specimens.

Each of the dihydropyrrolizine-containing species reported here possesses a unique complement of dihydropyrrolizines. Even when collected in widely separated areas (Mackay and Townsville) specimens of *D. hamatus hamatus* retained the same dihydropyrrolizines in the same relative concentrations. It is therefore possible that a species-specific composition of the hair-pencil secretions may contribute to maintaining the integrity of Danainae species.

The similarity in the structure of the dihydropyrrolizines found in the butterflies and the metabolites produced in mammals treated with pyrrolizidine alkaloids supports the possibility that the butterflies obtain the hair-pencil dihydropyrrolizines by transforming precursors found in their food plants[4]. Until recently pyrrolizidine or dihydropyrrolizine derivatives were not known to occur in the plant families to which the host plants of Danainae larvae belong – mostly the Asclepiadaceae, Apocynaceae and Moraceae. It has now been reported that 1-hydroxymethyl-7-oxo-6, 7-dihydro-5H-pyrrolizine (VII) occurs in *Urechites karwinsky* Mueller[9], which is the same family (Apocynaceae), sub-family (Apocynoideae) and tribe (Apocyneae) as the host plants of some Australian species of Danainae. The sub-family Apocynoideae is very closely related to the sub-family Cynanchoideae of the Asclepiadaceae in which most host plants of Australian *Danaus* species are found[10].

Zusammenfassung. Von 6 australischen Schmetterlingsarten der Untergruppe Danainae enthielten 4 Dihydropyrrolizine, dazu das bekannte Keton (I) und 2 verwandte Substanzen (II and III).

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[9] J. BORGES DEL CASTILLO, A. G. ESPANNA DE AGUIRRE, J. L. BRETON, A. G. GONZALES and J. TRUJILLO, Tetrahedron Lett. *1970*, 1219.

[10] We thank J. C. LE SOUEF, C. N. SMITHERS, A. D. and M. CHAPMAN and A. ATKINS for the collection of butterflies.

Catecholic Flavonoids from Soybean Flakes

In the course of our investigation of the spontaneous 'browning' or 'burning' of soybean flakes, we isolated an uncommon isoflavone glycoside from an extremely 'browned' sample.

The sample was extracted at room temperature with acetone containing 30% water. The dark brown extract was concentrated, methanol was added to precipitate peptides, the supernatant evaporated, dissolved in water and passed over a polyamide columm. After washing the columm with water till no more material was eluted, a 50% aqueous methanol eluent yielded a substance which could be recrystallized from hot water. It melted