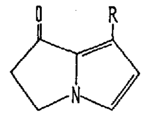
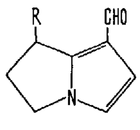
presence of 2 main components with the same chromatographic properties and colour reactions with Ehrlich's reagent as authentic samples of the ketone (I) and the hydroxyaldehyde (II). Reduction of the extract with sodium borohydride gave 2 products with Rf and Ehrlich colours identical with those of 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.

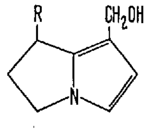
The extract from *Danaus affinis affinis* (Fab.) (15 males) contained 2 main Ehrlich positive components with Rf values and colour reactions identical with authentic samples of (I) and (III). The mass spectrum of the extract was consistent with a mixture of (I) and (III), and sodium borohydride reduction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



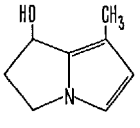
(I) R=CH_3
(VII) R-CH_2OH



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

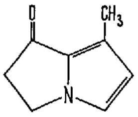
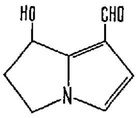
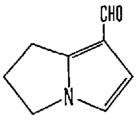


(IV) R=OH
(V) R=H



(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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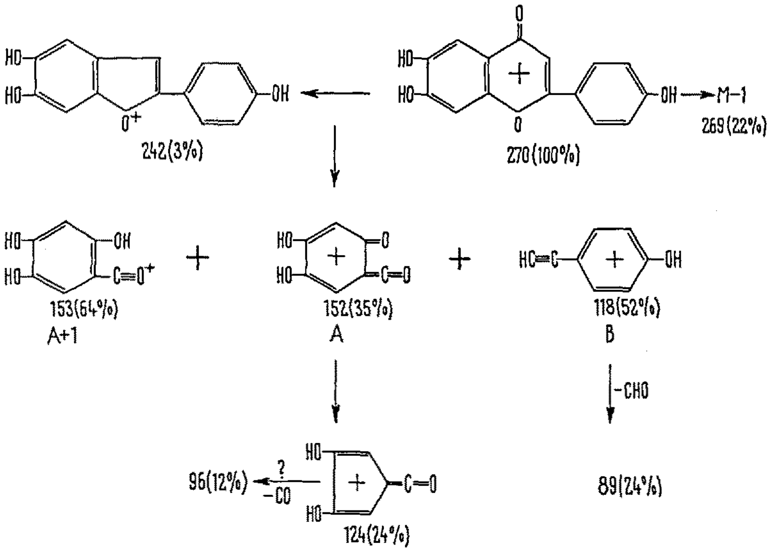
Catecholic Flavonoids from Soybean Flakes

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 with decomposition at 240°C and gave an intense green colour reaction with ferric chloride solution, indicating a free catechol group[1]. Elemental analysis fitted the composition $C_{21}H_{20}O_{10}H_2O$ (Fd. C 56.17; H 4.87; calculated C 56.01; H 4.92). The IR-spectrum showed absorptions at 3300–3420 (b); 1630–40, 1575, 1520 and 1253 cm^{-1}. The UV-spectrum showed absorptions at 260 and 327 nm. The spectral data compare very well with those given by McMURRY and THENG[2] for 6, 7, 4, trihydroxy isoflavone. From the spectral data and the elemental analysis we concluded that the substance was 6,7,4′ hydroxy isoflavone-4′-glycoside; the position of the glycosyl group was inferred from the fact that the reaction with ferric chloride indicated a free catechol function.

the transformation of 7, 4′ dihydroxy flavanon to daidzein as has been shown by GRISEBACH and ZILG[10].

If we assume that the 2, 3 double bond in the flavone was reduced by fungal action, the necessary flavanon would have been provided. The alternative route, involving fungal hydration of the double bond, followed by a retropinacol rearrangement is much less probable. Such a rearrangement has been shown to take place, in vitro, with catechuic acid tetra methyl ether, which is transformed into the corresponding isoflavane[11]. This has never been found to take place in vitro with flavones or flavanones and as BARZ and GRISEBACH[12] have shown, does not occur in the biosynthesis of biochanin A or formononetin either.



The aglycone of this compound had been isolated previously, by means of a similar method by GYORGY, NURATA and IKEHATA[3] from tempeh, a Japanese food consisting of fermented soybeans.

Investigating fresh soybean flakes in the same way, we did not come across this isoflavone glycoside but isolated a different catechol. It decomposed at 320°C and had IR-absorptions at 3140 and 3210 (b), 1655, 1632, 1612, 1490, 1253 and 1240 cm^{-1}. Its UV-spectrum had a single peak at 264 nm. Mass spectroscopy revealed a molecular ion of 270 (100%), fragments of 269 (M-1) (22%), 242 (M-28) (30%), 152 (A) (35%), 153 (A+1) (64%) and 118 (B) (52%), in addition to subfragments (Figure). This is the fragmentation pattern to be expected for 6,7,4′ trihydroxy flavone[4]; the flavone structure being indicated by the presence of the (M-28) fragment and the relative lack of prominence of the (M-1) fragment[5]. The compound, cursorily described by BARGELLINI and GRIPPA[6], has the same decomposition point and gives the same colour reaction.

The fact that neither we, nor GYORGY and his group[3], could isolate the isoflavone from fresh unfermented soybean meal or flakes, leads to the assumption that it was formed from the flavone by fungal action. It has already been postulated by ROBINSON[7] that isoflavones were formed in vivo by way of an arylmigration on a 2-aryl chromone skeleton. This assumption has received experimental support in the work of GRISEBACH[8] and his school. A flavanon is required as a starting molecule for this reaction[9]. Soybean seedlings are able to catalyze

Zusammenfassung. Isolierung zweier isomerer Vertreter der Flavongruppe aus Soyabohnenmehl: 6, 7, 4′Trihydroxyflavon aus frischem, Isoflavonglykosid aus gebräuntem Material.

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