less active than the corresponding K-region expoxide **7** in this test system[182]. K-region epoxides of noncarcinogenic hydrocarbons such as phenanthrene 9,10-oxide **6** and chrysene-5,6-oxide **179** were completely inactive[182]. Polycyclic arene oxides are active alkylating agents that bind to, and react with DNA, RNA and proteins[183–186]. Certain polycyclic arene oxides are potent mutagens in strains of *Salmonella*[187], in bacteriophages[188] and in a clone of chinese hamster cells[189], possibly because of interaction with DNA.

Arene oxides are important as metabolic intermediates capable of initiating tissue necrosis and carcinogenesis. Correlation of stability and reactivity with the structure of arene oxides will provide a sound basis for predictions of cytotoxicity. For example, alkylarene oxides which have low stability and rapidly rearrange to phenols, should not be cytotoxic or give diols[5,6]. In addition, phenols may be formed by oxygenases either directly or via intermediate arene oxides and this dualism may depend on the structure of the aromatic substrate. Compounds which form phenols directly by an insertion reaction would be expected to be nontoxic. The cytotoxic activity of intermediate arene oxides could probably be counteracted and offset by enhancing the rate of detoxification of such oxides, either through increases in levels of gluthatione or epoxide-hydrase. The present review indicates how efforts initiated to elucidate an unprecedented phenomenon, 'the NIH shift', have now opened up active research in the multidisciplinary area of formation, metabolism, toxicity, carcinogenicity and chemical reactivity of the novel labile metabolites known as arene oxides.

Zusammenfassung.

Nach der Isolierung des ersten Arenoxyds als labiler Zwischenverbindung im oxydativen Abbau von Naphthalin mit Lebermikrosomen besteht kein Zweifel mehr, dass im Stoffwechsel aromatischer Substrate ganz allgemein Arenoxyde obligatorische Primärprodukte sind, von denen sich durch enzymatische und nichtenzymatische Additionen und Umlagerungen zwangsläufig Dihydrodiole und (Prä-)Merkaptursäuren ableiten. Die Mono-Oxygenasen des Tier- und Pflanzenreichs einschliesslich der Pilze und Bakterien führen die Hydroxylgruppe unter Wanderung des ursprünglichen Substituenten ein, eine Umlagerung, die als *NIH-Verschiebung* bekannt wurde und als Beweis für das intermediäre Auftreten von Arenoxyden gültig ist. Die kurz- und langfristige Toxizität aromatischer Arzneimittel sowie die krebserregende Wirkung polyzyklischer aromatischer Kohlenwasserstoffe, wie Modellversuche andeuten, lässt sich von der Öffnung von Arenoxyden durch nukleophile Gruppen im Gewebe und kovalente Bindung an Biopolymere erklären.

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SPECIALIA

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Compounds of Papilionid Caterpillars (*Baronia brevicornis* S.)

In recent years the chemical study of insects has induced a big interest in that field, specially with the discovery of the metamorphosis hormones which play a vital role within the postembrionic development of the insect.

The defense mechanism of the caterpillars of butterflies of the family Papilionidae have been investigated recently[1], finding that the principal products everted by the defensive gland, the osmeterium, are two aliphatic acids, isobutyric and 2-methyl butyric acids, which are known to play the role of larvae protectors, especially from ants[2].

Since *Baronia brevicornis* Salv. is a singular specimen of the Mexican fauna and its philogenetic characters have been studied[3], therefore it was interesting to study the larvae from the chemical point of view. We wish to report now on some of the products found in the bodies of the caterpillars of *Baronia brevicornis* S.

The caterpillars were collected in km 23 of the road from Jojutla to Cuautla, Estado de Morelos, México, being in the 5th stage of its living cycle; in average, the weight per larvae was 350 mg.

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560 g of caterpillars were put in a round 2 liter 24/40 flask, killed with powdered dry ice, and the flask connected to a trap cooled with dry ice; the system was evacuated to 0.05 mm and kept at that pressure during 48 h in order to dry completely the larvae. The vapor trapped in the dry ice trap was extracted with hexane, evaporated and the oily residue (200 mg) analized directly by NMR, showing the spectrum that the composition of the mixture was the same as found before[1] (57:43) of isobutyric and 2-methyl butyric acids. The dried bodies were ground with chloroform in a Waring blendor and allowed to reflux for 4 h. The extract was filtered and evaporated to dryness in a rotavapor and the oily residue (57 g) was chromatographed on silica gel (250 g). The fractions eluted with benzene (13 g) showed by thin layer chromatography, a mixture of compounds, that were chromatographed on 350 g of alumina. From the fractions eluted with hexane, crystallized a white solid (90 mg), m.p. 52–53°, that resulted to be a mixture of 3 saturated hydrocarbons, $C_{25}H_{52}$, $C_{27}H_{56}$ and $C_{29}H_{60}$, characterized by IR-, NMR- and mass-spectrometry. From the fractions eluted with benzene, crystallized a white solid (60 mg), m.p. 82°, that on mass-spectrometry showed 4 molecular ions, M^+: 336, 364, 392 and 420 that had allylic protons in 3.6 ppm (δ) as seen in its NMR-spectrum. The elution of the column with benzene-ethyl acetate 90:10, a complex mixture of triglycerides was obtained (2 g) and 50 mg of a crystalline solid, m.p. 146°, that was characterized as cholesterol by comparison of its IR-, NMR-, mass spectra and its chromatographic (TLC) behavior with an authentic sample of cholesterol.

Finally, the fractions eluted with ethyl acetate yielded a mixture of 7 g of 2 monounsatured acids, M^+: 256 and 284 and palmitic and stearic acids in a approximately 25% each.

Resumen. Se describe la naturaleza de algunos de los componentes principales que se encuentran en la oruga *Baronia brevicornis S.*

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The Structure of Three Isomers of Monodeacetylfusicoccin

Thin layer chromatography of culture filtrates of *Fusicoccum amygdali* Del. has shown[1] that fusicoccin (I), the main phytotoxic compound produced by this phytopathogenic microorganism[2–4], is consistently accompanied by a series of co-metabolites. The major by-products are isofusicoccin (II), monodeacetylfusicoccin (III) and dideacetylfusicoccin (IV), which are also formed, together with allofusicoccin (V), on incubation of fusicoccin at neutral or slightly alkaline pH values[1]. Their structural identification has been reported in previous papers[1,5].

Further work concerned with the isolation of minor by-products and with the structure determination of three of them is described here.

Extensive chromatographic fractionations on silica gel columns (Kieselgel S-HR, Macherey and Nagel) of the residue left in ethylacetate after crystallization of fusicoccin showed that some of the spots detected on thin layer chromatograms (indicated in a previous paper[1] as F-II, F-III..., F-VI, in order of decreasing mobilities) were due to more than one compound. In particular, the following results were obtained: F-II was a mixture of allofusicoccin (F-II/1) and minute amounts of a new compound (F-II/2); F-III and F-IV contained only isofusicoccin and monodeacetylfusicoccin, respectively; material initially behaving as spot F-V gave 3 groups of homogeneous fractions (F-V/1, F-V/2, F-V/4) and a 4th group corresponding to a mixture of a new compound (F-V/3, present only in traces) with F-V/2 and F-V/4; F-VI corresponded to a single substance; F-VII was entirely composed of dideacetylfusicoccin; furthermore, a new substance (F-VIII) was detected in a group of fractions eluted after F-VII. Compounds F-V/1, F-V/2, F-V/4, F-VI and F-VIII were isolated as pure substances and submitted to a detailed study. All of them are D-glucosides, as shown by the positive test with glucose oxidase after acid hydrolysis, and are oxidizable with periodate.

Compounds F-V/2, F-V/4 and F-VI yielded triacetylfusicoccin (VI) on acetylation[6] and dideacetylfusicoccin (IV) on deacetylation with alkali, thus indicating that their structures are very closely related to fusicoccin. Their NMR-spectra[7] demonstrated, besides other features characteristic of fusicoccin and related compounds, the presence of a single *O*-Ac group. Their mass spectra showed that they had molecular formula $C_{34}H_{54}O_{11}$ (M^+ 638), also confirmed by elementary analyses. Ions at *m/e* 366 (aglycone) and 205 (monoacetylglucosyl) in the mass spectra of F-V/2 and F-VI located in both compounds the *O*-Ac on the sugar moiety. A strong ion at *m/e* 408 in the mass spectrum of F-V/4 indicated that this substance carries the *O*-Ac group on the aglycone. The esterification site in each of the 3 above-mentioned monoacetates was defined by NMR- and NMDR-spectroscopy.

Compound F-V/2, m.p. 87–90° and $[\alpha]_D^{25}$ + 15.0 (c = 0.65), in d_6-acetone (60°) shows a *dd* (1H) centred at 4.70 δ with (eq) (ax) and (ax) (ax) couplings (J = 4 and 9 Hz), which collapses to a *d* on irradiation at 4.91 δ (1H, *d*, J = 4 Hz: anomeric proton, partially overlapping the

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[7] NMR-spectra were recorded on a Varian HA-100 apparatus with TMS as internal reference. Optical rotations were measured with a Perkin-Elmer 141 polarimeter on ethanolic solutions. Mass spectra were recorded on an AEI MS-902 spectrometer. Melting points are uncorrected. All compounds gave satisfactory elementary analyses.