SESQUITERPENE LACTONES OF *Pyrethrum pyrethroides*.

II. PYRETHROIDIN

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A new sesquiterpene lactone, pyrethroidin, and a known one — 8-deoxycumambrin B — have been isolated from the epigeal part of the plant *Pyrethrum pyrethroides*. The structure of 4,10-dihydroxy-1,5α,7α(H),6β(H)-guaia-2,11(13)-dien-6,12-olide has been suggested for pyrethroidin.

We have previously reported the isolation of cumambrins A and B from *Pyrethrum pyrethroides* (Kar. et Kir.) B. Fedtsch. [1]. Continuing a study of the epigeal part of this plant for its sesquiterpene lactones, we have isolated another two lactones.

Lactone (I) was identified from its IR, mass, and PMR spectra as 8-deoxycumambrin B [2]. Lactone (II) proved to be a new compound, and we have called it pyrethroidin.

The IR spectrum of (II) contained absorption bands at (cm^{-1}) 3420-3460 (hydroxy groups), 1740, 1662 (C=O and C=C in a conjugated γ-lactone system), and 1630 (isolated double bond). The UV spectrum of the lactone, with a maximum at 206 nm (log ε ε 4.35), likewise indicated the given nature of the double bond.

The mass spectrum of pyrethroidin showed the peak of the molecular ion with m/z 264 (M^+, 0.43%), the peaks of ions with m/z 246 ($M - H_2O$) (18%) and 228 ($M - 2H_2O$) (35%) due to the ejection of one and two molecules of water, respectively, and also fragments with m/z 189 ($C_{12}H_{13}O_2$) (18%), 188 ($C_{12}H_{12}O_2$) (32%), 175 ($C_{11}H_{11}O_2$) (24%), and 173 ($C_{11}H_9O_2$) (15%), which are characteristic for the fragmentation of guanolides under electron impact [3].

The hydroxy groups of (I) did not undergo acetylation with acetic anhydride in pyridine, which shows their tertiary nature.

The assignment of the signals in the PMR spectra of pyrethroidin was made with the aid of double resonance; singlets at 1.40 and 1.04 ppm (3 H each, 2 $C\underline{H}_3{-}C{-}OH$ at C-4 and C-10, respectively), triplets at 2.66 ppm (1 H, H-5, Σ^3J = 20 Hz), doublet with considerably broadened components at 3.19 ppm (1 H, H-1, $^3J \approx 9.8$ Hz), quartet at 4.20 ppm (1 H, H-6, $^3J \approx 9.5$ and 11.0 Hz), and two doublets at 5.50 and 6.20 ppm (1 H each, $C{=}C\underline{H}_2$ at a lactone ring, $^4J \approx 2.9$ and 3.2 Hz, respectively). One-proton quartets at 5.76 and 5.92 ppm were assigned to olefinic protons, and the spin-spin coupling constant between them was 6 Hz, which is characteristic for a double bond present in a five-membered ring [4]. Each of them also interacted with H-1, vicinally with $^3J \approx 2.5$ Hz and in the allyl manner with $^4J \approx 1.8$ Hz. These facts permitted the unambiguous establishment of the position of the isolated double bond in the pyrethroidin molecule between carbons C-2 and C-3.

The quartet nature of the splitting of the H-6 proton was due to its interaction with H-5 ($^3J \approx 11.0$ Hz) and H-7 ($^3J \approx 9.5$ Hz), and these facts showed the trans linkage of the lactone ring with the basic skeleton at the C-6 and C-7 atoms. This was also shown by the presence of a negative maximum in the circular dichroism spectrum of pyrethroidin at 255 nm with $|\theta|$ — 2160 (methanol) [5].

The value of $^3J \approx 9.8$ Hz between H-1 and H-5 that was found could correspond equally to their mutual orientations as cis (θ ~ 0°) and trans (θ ~ 160-180°). This circumstance eliminated the possibility of an unambiguous choice between them. However, as stated above, the plant under investigation contained, in addition, to pyrethroidin, cumambrins A and B and 8-deoxycumambrin B, and the cis linkage of rings A and B has been established for the latter

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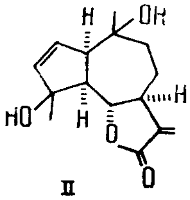
compounds [2]. In view of the possible biogenetic link between these compounds, it may be assumed that the cis linkage of rings A and B also exists in the pyrethroidin molecule.

The facts given above permit us to propose for pyrethroidin the structure of 4,10-dihydroxy-1,5α,7α(H),6β(H)-guaia-2,11(13)-dien-6,12-olide and to determine the relative stereochemistries of a number of its asymmetric centers.



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EXPERIMENTAL

UV spectra were taken on a Specord UV-Vis spectrometer, IR spectra on a UR-20 instrument (KBr), mass spectra on an MKh-1303 spectrometer and PMR spectra on a JNM-4H 100 spectrometer (JEOL) in $CDCl_3$, δ, ppm, 0 — HMDS.

Isolation of 8-Deoxycumambrin B (I) and Pyrethroidin (II). The epigeal part of *Pyrethrum pyrethroides* was collected in June, 1983 (Hissar range, Tadzhik SSR). The air-dried comminuted plant mass (20 kg) was exhaustively extracted with chloroform. The residue obtained after the chloroform had been distilled off was treated in stages with 40%, 50%, and 70% aqueous ethanol. The lactones were extracted from the 40% aqueous ethanolic solution with hexane, chloroform, and ethyl acetate. The chloroform extract (38 g) was separated by chromatography on neutral alumina (activity grade IV) in a ratio of 1:30. The column was washed with hexane and with hexane—ethyl acetate (9:1) with a subsequent increase in the concentration of ethyl acetate.

Fractions 2-4 yielded a compound with mp 117°C (ethyl acetate—hexane), composition $C_{15}H_{20}O_3$, which was identified as 8-deoxycumambrin B [2].

The resin eluted by the hexane—ethyl acetate (3:2) system was rechromatographed on a column of silica gel. Elution with chloroform—acetone (19:1) yielded pyrethroidin, $C_{15}H_{20}O_4$, mp 180-182°C (ethyl acetate—hexane), $[\alpha]_D^{22}$ − 105° (c 0.33; methanol), $\lambda_{max}^{C_2H_5OH}$: 206 nm (log ε 4.35).

Mass spectrum, m/z (%): 264 (M^+, 0.4), 249 (32), 246 (18), 231 (25), 228 (35), 226 (16), 213 (25), 206 (19), 204 (16), 204 (16), 203 (45), 189 (16), 188 (32), 185 (38), 175 (25), 173 (16), 170 (16), 169 (16), 168 (16), 167 (83), 163 (22), 161 (36), 160 (32), 147 (32), 145 (45), 143 (45), 133 (40), 131 (32), 129 (33), 125 (38), 117 (44), 109 (100).

SUMMARY

A new sesquiterpene lactone pyrethroidin and a known one — 8-deoxycumambrin B — have been isolated from the epigeal part from *Pyrethrum pyrethroides*. The structure of 4,10-dihydroxy-1,5α,7α(H),6β(H)-guaia-2,11(13)-dien-6,12-olide has been proposed for pyrethroidin.

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