

determined by oxidative degradation with hydrogen peroxide, and it was found that the carbohydrate substituent of the substance was identical with rutinose [3]. The sizes of the oxide rings of the sugar residues and the forms of the bonds were determined from the results of IR spectroscopy and polarimetric analysis.

The experimental results and also a comparison with an authentic sample indicated that flavonoid (III) was identical with rutin.

In view of the fact that the conditions of growth affect the synthesis and amount of organic compounds in plants, we determined the sum of the flavonoids quantitatively. In the plants that we investigated it was 9 $\mu\text{g/g}$ of raw mass of the leaves. This is the first time that the flavonoids of the leaves of the cotton plant of variety Tashkent 1 have been studied.

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SESQUITERPENE LACTONES OF *Pyrethrum pyrethroides*.

PYRETHROIDININ

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UDC 547.314+582.998

From the total chloroform extract of *Pyrethrum pyrethroides* (Kar. et Kir.) B. Fedtsch. [1] we have isolated a new sesquiterpene lactone with the composition $\text{C}_{15}\text{H}_{20}\text{O}_4$, mp 170–172°C (ethyl acetate–hexane) $[\alpha]_D^{22} +850^\circ$ (c 0.8; ethanol), which we have called pyrethroidinin. Its IR spectrum had absorption bands at 3360–3460 cm^{-1} (OH group), and 1770, 1670, and 1630 cm^{-1} (C=O, α,β -unsaturated γ -lactone conjugated with an isolated C=C bond). The UV spectrum was characterized by a maximum at $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 204 nm ($\log \epsilon$ 4.27). The circular dichroism spectrum of this compound ($\text{C}_2\text{H}_5\text{OH}$) showed a negative Cotton effect at 261 nm ($\Delta\epsilon = -0.57$) and a positive one at 208 nm ($\Delta\epsilon = 14.7$).

The mass spectrum of pyrethroidinin had the peak of the molecular ion with m/z 264 ($\text{M}^+ - 34\%$), and the peaks of ions with m/z 246 [$\text{M} - \text{H}_2\text{O}$] (365) and 228 [$\text{M} - 2\text{H}_2\text{O}$] (8.4%), due to the ejection of 1 and 2 molecules of water, and also fragments with m/z (%): 249 [$\text{M} - \text{CH}_3$] (3), 229 (3.9), 223 (6.9), 218 [$\text{M} - \text{CO} - \text{H}_2\text{O}$] (6.4), 213 [$\text{M} - 2\text{H}_2\text{O} - \text{CH}_3$] (23.5), 206 (8.9), 205 (8.4), 204 (9.9), 203 [$\text{M} - \text{H}_2\text{O} - \text{CH}_3 - \text{CO}$] (34.6), 194 (5), 193 [$\text{M} - \text{C}_4\text{H}_7\text{O}$] (18), 191 [$\text{M} - \text{C}_4\text{H}_9\text{O}$] (6.9), 190 (5.9), 189 [$\text{C}_{12}\text{H}_{13}\text{O}_2$] (20), 188 [$\text{C}_{12}\text{H}_{12}\text{O}_2$] (50), 185 [$\text{M} - 2\text{H}_2\text{O} - \text{CH}_3 - \text{CO}$] (15), 177 (54), 176 (14), 175 [$\text{C}_{11}\text{H}_{11}\text{O}_2$] (25), 173 [$\text{C}_{11}\text{H}_9\text{O}_2$] (8), 149 (100), etc, which are characteristic for the fragmentation of guaianolides under electron impact [2, 3].

The PMR spectrum of pyrethroidinin ($\text{C}_5\text{D}_5\text{N}$, 0 – HMDS) was characterized by the following signals (ppm): 1.00 (3 H, s, $\text{CH}_3 - \text{C} - \text{OH}$ at C-10); 2.06 (3 H, br.s, $\text{CH}_3 - \text{C} = \text{C}$); 3.39 (1H, m, H-7); 4.60 (1 H, br.d, H-6); 5.32 and 6.14 (1 H each, d, $^4\text{J} = 3.1$ and 3.4 Hz, respectively, 2 H-13); 5.75 (1 H, s, tertiary OH group); 6.24 (1 H, d, $^3\text{J} = 6$ Hz, secondary OH group). At 4.80 ppm there was a considerably broadened singlet which was converted in the presence of CD_3OD into a doublet with broadened lines having $^3\text{J} = 7.4$ Hz. Consequently, this signal belongs to a proton (H-3) located geminally to a secondary OH group.

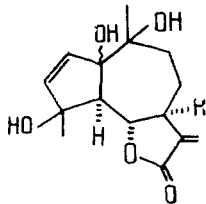
The presence of a methyl group on a double bond, of a $\text{CH}_3 - \text{C} - \text{OH}$ grouping, of doublet splitting of the signal of the lactone proton with $^3\text{J} = 10.9$ Hz, and the absence of an olefinic proton unambiguously showed the position of the isolated double bond in the guaiane structure of pyrethroidinin at C-4 and C-5, of a tertiary OH group at C-10, and of a trans-linked lactone ring at C-6 and C-7.

The values of the chemical shifts of the protons of the exocyclic methylene group of the lactone ring indicated the absence of a hydroxy substituent at C-8. The broadening of the

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodnikh Soedinenii*, No. 6, pp. 792–793, November–December, 1984. Original article submitted July 2, 1984.

H-3 and H-6 signals was due to homoallyl spin-spin coupling between them ($J \sim 1$ Hz) and to allyl coupling with the protons of a methyl group at a double bond ($J \sim 1$ Hz), as has been observed in the case of cyclopumilin-10 β -hydroxyguaia-4,13-dien-6,12-olide [4]. The structure of the splitting of the signal at 4.80 ppm mentioned above indicates a vicinal coupling of a proton geminal to a secondary OH group with not more than two protons. From this it followed that the secondary hydroxy group was located at C-3.

The facts given above taken all together permit the structure of pyrethroidinin to be established as 3,10-(di)hydroxy-6 β (H)m7 α (H)-guaia-4,11(13)-dien-6,12-olide.



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STRUCTURE OF SANCHILLIN

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UDC 547.314

We have previously [1] reported the isolation from the epigeal part of *Achillea santolina* L., together with leucomisin, austriacin, chrysartemin B, and santachin, of a lactone (V) with the composition $C_{15}H_{10}O_5$, mp 233°C (acetone), M^+ 280, R_f 0.5 silica gel; benzene-ethanol (9:1). This lactone is new and we have called it sanchillin.

Sanchillin is readily soluble in chloroform and pyridine and sparingly soluble in benzene, acetone, and ether, and it readily polymerizes in ethanol and on boiling in benzene. When the lactone was treated with selenium, the reaction mixture acquired a blue color, which is characteristic for compounds of the guaiane series. This was confirmed by the composition and by the presence of a peak with m/z 111 in the mass spectrum [2].

The IR spectrum of the compound (KBr tablets) showed absorption bands at (cm^{-1}) 3325-3480 (hydroxy groups), 1750 and 1660 ($C=O$ and $C=C$ in a conjugated γ -lactone system), and 1630 (isolated $C=C$ bond).

In the PMR spectrum of sanchillin (C_5D_5N , 0 - HMDS, $H_0 = 100$ MHz, doublets with an intensity of 1 H each at 5.98 and 6.23 ppm corresponded to two olefinic protons interacting vicinally in the manner of an AB system with $^3J = 5.9$ Hz. The value of the spin-spin coupling constant showed that the isolated double bond was present in a five-membered ring [3-5], which unambiguously indicated that sanchillin belonged to the guanolide group. In such a skeleton, the double bond can be formed only at C-2 and C-3.

There were broad singlets of 1 H each at 5.50, 6.38, and 6.57 ppm which broadened even more and shifted upfield with a rise in the temperature of the solution under investigation,

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodnikh Soedinenii*, No. 6, pp. 793-794, November-December, 1984. Original article submitted July 2, 1984.