A SESQUITERPENE LACTONE OF CYCLACHAENA XANTHIFOLIA—ANHYDROCORONOPILIN

V. I. Novikov, F. N. Forostyan, and D. P. Popa

Khimiya Prirodnykh Soedinenii, Vol. 6, No. 1, pp. 29–31, 1970

UDC 547.913

From the racemes of C. xanthifolia Fresen. we have isolated the sesquiterpene lactam anhydrocoronopilin (I), $C_{15}H_{18}O_3$, mp 120–122° C (from ether), $[\alpha]_D^{20}$ −60° (chloroform), identical with the product of the dehydration of the pseudoguaianolide coronopilin (II). The structure of $\Delta^{1(2)}$-anhydrocoronopilin has been proposed for it provisionally [1].

In the dehydration of II the formation of a double bond is theoretically possible at either C_1—C_2 or at C_1—C_{10}. The possibility is not excluded that the ketolactone I consists of an isomeric mixture of substances with the double bond in the two positions mentioned.

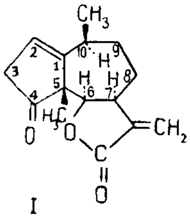
We have investigated the position of the double bond in the lactone I by dehydrating the products of the reduction and hydrogenation of coronopilin with various agents capable of splitting out water. Under severe conditions of the hydrogenation of II over $Pd/SrCO_3$ in ethanol, dihydroisoparthenin (III) was formed. The dehydration of the latter with P_2O_5 in benzene led to an anhydro derivative (IV) with the composition $C_{15}H_{18}O_3$, mp 153–155° C, $[\alpha]_D^{20}$ +8° (chloroform).

In its physicochemical constants and IR spectrum, compound IV is identical with the anhydrodihydroisoparthenin described in the literature, which has the double bond at C_1—C_{10} [2].

The reduction of II with zinc in acetic acid gave dihydrocoronopilin (V) with mp 186–188° C (from acetone–ether). Dehydration of the latter with thionyl chloride in pyridine yielded anhydrodihydrocoronopilin (VI), $C_{15}H_{20}O_3$, mp 145–146° C (from ether), $[\alpha]_D^{20}$ −33° (chloroform). According to its IR spectrum, the dehydration product does not contain a hydroxyl group, and it shows absorption bands characteristic for a γ-lactone and a cyclopentanone (1745, 1405 cm^{-1}). The properties mentioned for anhydrodihydrocoronopilin agree well with those of the product of reduction with zinc in acetic acid of the sesquiterpene lactone parthenin with the double bond at C_1—C_2 [2].

When anhydrocoronopilin was reduced with zinc in acetic acid, compound VII was obtained. The reduction product, VII, was identical in its physicochemical constants, IR spectrum, and mixed melting point with anhydrodihydrocoronopilin.

Consequently, the dehydration of dihydrocoronopilin takes place with the formation of a double bond at C_1—C_2, which proves the structure proposed previously for anhydrocoronopilin. The identity of anhydrodihydrocoronopilin with the product of the reduction of parthenin shows the β-configuration of the methyl group at C_5 and C_{10} and confirms the structure (I) proposed previously for anhydrocoronopilin.



I

EXPERIMENTAL

Dihydroisoparthenin (III). One gram of coronopilin in 30 ml of ethanol was hydrogenated with 200 mg of 5% $Pd/SrCO_3$ under a pressure of 2 atm of hydrogen at 29° C for 24 hr. The solvent was distilled off and the residue was purified with 5 g of alumina (activity grade IV) with chloroform. The chloroform eluates were evaporated and the reaction product was crystallized from benzene–petroleum ether (1 : 1). This gave 0.85 g of III with mp 191–193° C. IR spectrum (UR-10, KBr), cm^{-1}: 3490 (—OH), 1745, 1408 (γ-lactone and cyclopentanone), 1655 (double bond).

Anhydrodihydroisoparthenin (IV). A solution of 0.8 g of III in 20 ml of anhydrous benzene was treated with 2 g of P_2O_5, and the mixture was left for 2 hr. The phosphorus pentoxide was filtered off and the benzene filtrate was evaporated. The residue was dissolved in chloroform and the solution was chromatographed on 12 g of alumina (activity grade II) in the benzene–ether (1 : 2) system. The eluates were evaporated and the residue was crystallized from ether, giving 0.27 g of IV, $C_{15}H_{18}O_3$, mp 153–155° C, $[\alpha]_D^{20}$ +8° (c 1.1; chloroform). IR spectrum, cm^{-1}: 1750 (γ-lactone and cyclopentanone), 1674 ($>C=C<$) cm^{-1}.

Dihydrocoronopilin (V). A solution of 3 g of coronopilin in 100 ml of 85% acetic acid was treated with 18 g of zinc dust, and the mixture was left for 72 hr. The excess of zinc dust was filtered off and the acetic acid was distilled off in vacuum. The residue was treated with 100 ml of chloroform, and the chloroform extracts were washed with 20 ml of 10% sodium carbonate solution and then with water and were dried and evaporated. The residue was crystallized from acetone–ether (1 : 1), giving 2.2 g of dihydrocoronopilin, mp 186–188° C. IR spectrum, cm^{-1}: 3485 (–OH), 1770 (γ-lactone), 1745, 1407 (cyclopentanone).

Anhydrodihydrocoronopilin (VI). A solution of 0.85 g of dihydrocoronopilin in 10 ml of dry pyridine was cooled to 0° C, and a solution of 0.85 ml of thionyl chloride in 5 ml of dry pyridine, also cooled to 0° C, was added dropwise. After 10 min, the reaction mixture was poured into 50 ml of ice water. The reaction products were extracted with chloroform; the 80 ml of chloroform extract was washed with 30 ml of 15% HCl solution and then with water and was dried and evaporated. The residue was purified on 5 g of alumina (activity grade II) in the chloroform–benzene (7 : 3) system. The eluates were evaporated and the residue was crystallized from ether, giving 0.45 g of VI with mp 145–146° C, $[\alpha]_D^{20}$ –33° (c 3.0; chloroform). IR spectrum, cm^{-1}: 1745, 1408, 1380, 1210, 1180, 980.

Reduction of I with Zn/HAc. A solution of 0.7 g of anhydrocoronopilin in 35 ml of 90% acetic acid was treated with 5 g of zinc dust. The mixture was left for 72 hr. The zinc dust was filtered off. The acetic acid was distilled off under vacuum. The residue was treated with 50 ml of chloroform, and the chloroform extract was washed with 5% sodium carbonate solution (20 ml) and was dried and evaporated. The residue was crystallized from ether, giving 0.45 g of substance VII with mp 144–146° C (no depression of the melting point was found in a mixture with anhydrodihydrocoronopilin), $[\alpha]_D^{20}$–35° (c 3.3; chloroform). IR spectrum, cm^{-1}: 1745, 1408, 1380, 1210, 1180, 980.

CONCLUSIONS

It has been shown that the dehydration of the sesquiterpene lactone coronopilin with $SOCl_2$ forms $\Delta^{1(2)}$-anhydrocoronopilin. The configuration of the methyl groups at C_5 and C_{10} in anhydrocoronopilin has been established by analogy with the conversion products of the pseudoguaianolide parthenin.

REFERENCES

1. V. I. Novikov, Yu. N. Forostyan, and D. P. Popa, KhPS [Chemistry of Natural Compounds], 5, no. 6, 1969.
2. W. Herz, H. Watanabe, M. Miyazaki, and Y. Kishida, J. Am. Chem. Soc., 13, 2601, 1962.

13 November 1968

Zaporozh'e Branch, Donetsk Institute of Soviet Trade