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AN ISOMER OF CORONOPILIN

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As a result of a chemical investigation of the racemes of Cyclachaena xanthifolia Fresen. (rag sumpweed) we have have isolated a sesquiterpene lactone (I) $C_{15}H_{20}O_4$, with mp 164–166° C, $[\alpha]_D^{20}$ +47.7° (chloroform). Its IR spectrum exhibits absorption bands at 820 and 1660 cm^{-1}, corresponding to a double bond in a lactone ring [1]; strong absorption in the 1408 and 1745 cm^{-1} regions may be ascribed to the carbonyl group of a γ-lactone and of a cyclopentanone [2], and the band at 3490 cm^{-1} confirms the presence of a hydroxyl group in the substance. The fingerprint sections of the IR spectra of the ketolactone I and of the (−)-coronopilin that we have isolated from this plant previously [3] coincide. The IR spectrum of substance I shows the absence of conjugated double bonds from its molecule.

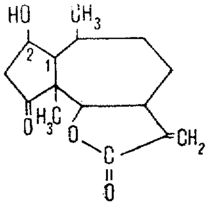
Dehydration [4] of the lactone gave a product $C_{15}H_{18}O_3$ with mp 144–146° C in the IR spectrum of which there were absorption bands at (cm^{-1}): 1585 (double bond in a five-membered ring) [5], 820 and 1660 (double bond of a γ-lactone), 1408 and 1720 (C=O of a cyclopentanone), and 1770 (γ-lactone). There was no OH-group absorption.

The UV spectrum of the dehydration product contains maxima at 219 and 320 mμ (log ε 4.18 and 1.70, respectively), which are characteristic for carbonyl groups in conjugation with a double bond [6].

The results of dehydration give grounds for assuming that the five-membered ring of I contains, in addition to a hydroxyl group, a carbonyl group the absorption bands of which in the IR spectrum are present in the 1720 and 1745 cm^{-1} regions, which is characteristic of five-membered, and not six- or seven-membered, ketones.

The lactone I investigated contains another carbonyl group. The reduction of I with sodium borohydride gave a noncrystalline chromatographically homogeneous product the IR spectrum of which had absorption bands at 3490 cm^{-1} (hydroxyl) and 1720 cm^{-1}(C=O of a cyclopentanone). This result of reduction shows that the molecule of I contains a lactone group undergoing reduction under these conditions. From the position of the absorption bands in the IR spectrum due to it (1770, 1745 cm^{-1}), the group can only be a γ-lactone group.

On the basis of what has been said above, a preliminary conclusion can be drawn concerning the structure of the carbon skeleton of this compound and it may be assumed that the hydroxyl group is located in the five-membered ring at C_2. The substance obtained is a structural (+) isomer of (−)-coronopilin, and has the structure I.



Experimental

We investigated the racemes of C. xanthifolia collected in the Zaporozhie region in August 1967. The preparative separation of the isomers was carried out on a plate (62 × 17.5 cm) with a thin layer (0.7 mm) of alumina (activity grade IV) in system 1) chloroform–benzene–methanol (20 : 20 : 2), qualitative separation being carried out in systems 2) ethyl acetate–benzene–ethanol (20 : 20 : 0.8); 3) carbon tetrachloride–chloroform–ethanol (10 : 30 : 1); and 4) benzene–acetone–ethanol (40 : 10 : 1.5). On a thin layer of silica gel G of type KSK, chromatography was carried out in system 5); benzene–acetone (4 : 1).

Isolation of the combined sesquiterpene lactones. The air-dry racemes (12 kg) were shaken repeatedly with water saturated with chloroform (1 : 400) (5 × 20 *l*). The aqueous extract was treated with chloroform (5 × 5 *l*). The dried chloroform extract was evaporated to a small residue (80 g). This was dissolved in benzene (300 ml) and the solution was treated with petroleum ether (200 ml). The crystals that deposited were washed with cold benzene and were purified by three crystallizations from benzene–petroleum ether (2 : 1). This gave 54 g (0.45%) of a mixture of lactones consisting of four substances with R_f 0.14, 0.23, 0.55, and 0.65 in system 1, 0.16, 0.33, 0.57, 0.85 (2); 0.19, 0.34, 0.63, 0.76 (3); 0.26, 0.37, 0.65, 0.83 (4), and 0.32, 0.65, 0.80, 0.90 (5).

Micro preparative separation of the combined lactones [7]. A 20% chloroform solution of the combined lactones was deposited by means of a microsyringe in 2.5-ml (0.5-g) portions on the starting line in the form of a band. Chromatography was carried out in system 1 and the plates were dried at 40–50° C. The spots revealed in UV light were transferred to glass filters and the alumina was eluted with hot benzene (150 ml). The benzene solutions were evaporated to 25 ml, and then the addition of 15 ml of petroleum ether in each case yielded the following crystalline substances: 0.25 g of (−)-coronopilin, identified by its physicochemical constants, with R_f 0.23 (1), and 0.19 g of the (+)-isomer of coronopilin (I) with R_f 0.14, 0.16, 0.19, 0.26, 0.32 (1–5, respectively).

Found, %: C 68.13, 68.14; H 7.74, 7.62; mol. wt. 264 (mass spectrometry). Calculated for $C_{15}H_{20}O_4$, %: C 68.16; H 7.63; mol. wt. 264.1.

Dehydration [8]. A solution of 0.2 g of the (+)-isomer of coronopilin in 5 ml of a mixture of acetic anhydride and acetic acid (1 : 1) was left at room temperature for 24 hr. The dehydration product was extracted by the usual method and deposited on a column of 20 g of alumina (activity grade II). The dehydration product was eluted with petroleum ether–chloroform (70 : 30). The evaporated eluates deposited 0.15 g of a crystalline substance with R_f 0.55, 0.63 (systems 1 and 3, respectively).

Found, %: C 73.28, 73.15; H 7.66; 7.52; mol. wt. 245 (mass spectrometry). Calculated for $C_{15}H_{18}O_3$, %: C 73.25; H 7.32; mol. wt. 245.7.

Reduction of I. A solution of 0.5 g of the (+)-isomer of coronopilin (I) in 50 ml of 50% methanol was treated with 0.6 g of sodium borohydride. The mixture was left at 20° C for 24 hr, after which it was evaporated to small bulk in vacuum. A noncrystalline chromatographically homogeneous product was obtained.

Conclusions

From the racemes of C. xanthifolia Fresen. have been isolated a sesquiterpene lactone $C_{16}H_{20}O_4$, the structural (+)-isomer of (−)-coronopilin, which has not been studied previously; structure I has been proposed for it.

REFERENCES

1. W. Herz and H. Watanabe, J. Am. Chem. Soc., **81**, 1088, 1959.
2. N. P. Kir'yalov et al., KhPS [Chemistry of Natural Compounds], 2, 93, 1966.
3. L. Farkas, M. Norgadi, V. Sudarsanam, and W. Herz, J. Org. Chem., **10**, 3288, 1966.
4. C. Enzell, Acta Chem. Scand., **15**, 1303, 1961.
5. W. Herz and G. Högenauer, J. Org. Chem., **26**, 5011, 1961.
6. R. W. Woodward, J. Am. Chem. Soc., **63**, 1123, 1941.
7. E. Stahl, Dünnschicht-Chromatographie: ein Laboratoriumshandbuch [Russian translation], Moscow, p. 22, 1965.
8. M. A. Chirkova et al., KhPS [Chemistry of Natural Compounds], 3, 86, 1967.

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