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ISOLATION OF GAILLARDIN FROM INULA OCULUS-CHRISTI

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From the epigeal part of Inula oculus-Christi L. (Christeye inula) gathered in the Azerbaidzhan SSR on June 22, 1968, we have isolated (yield 0.1%) a lactone (I) with the composition $C_{17}H_{22}O_5$, mp 197–198.5° C (from ethanol), $[\alpha]_D^{18}$ −11.87° (c 3.77; chloroform); IR spectrum, ν_{max}, cm^{-1}: 3520 (OH), 1770 and 1661 (α, β-unsaturated γ-lactone), 1720 and 1250 ($OCOCH_3$).

In the NMR spectrum of I there is a singlet at 1.31 ppm ($CH_3—C—OH$); a broadened singlet at 1.75 ppm ($CH_3—C═C$); a singlet at 2.09 ppm ($CH_3—OCO$); a doublet with broadened components at 4.51 ppm (lactone proton); a broadened singlet at 5.24 ppm (ester proton); a broadened singlet at 5.87 ppm (vinyl proton); and a pair of doublets at 5.54 and 6.20 ppm (J = 3 Hz) (exocyclic methylene in conjugation with a lactone carbonyl).

The hydrogenation of I in the presence of Pt (from PtO_2) in the ethanol gave a tetrahydro derivative (II), $C_{17}H_{26}O_5$, with mp 175.5–177.5° C (from ethanol); ν_{max}, cm^{-1}: 3520, 1775, 1725, and 1260.

The hydrolysis of II in 2.5% K_2CO_3 solution at 85–90° C for 2.5 hr led to a desacetyltetrahydro derivative (III), $C_{15}H_{24}O_4$, with mp 193.5–195° C (from ethanol); ν_{max}, cm^{-1}: 3480 (OH), 1768 (γ-lactone).

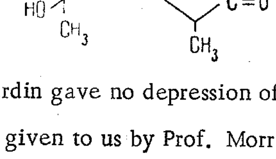
The oxidation of III with chromic anhydride in 90% acetic acid at 5° C for a day gave the desacetyldehydrotetrahydro derivative IV, $C_{15}H_{22}O_4$, with mp 196.5–199° C (from benzene); ν_{max}, cm^{-1}: 3560 (OH), 1765 (γ-lactone), 1750 (cyclopentanone).

The dehydrogenation of I over Se at 300–370° C for 1 hr gave chamazulene.

It followed from the results obtained that the substance isolated from the plant is a sesquiterpene lactone of the azulene series.

On comparing the constants of our lactone with those given in the literature, we noted a similarity to gaillardin—a cytotoxic sesquiterpene lactone from Gaillardia pulchella Foug. [1]. However, the previous authors did not succeed in obtaining a tetrahydro derivative of gaillardin while in our experiment it crystallized readily. The desacetyl derivative of our lactone had mp 143–145° C (form desacetylgaillardin, mp 149–151° C).

The NMR spectra of the lactone that we isolated and of its tetrahydro derivative practically coincided with those of gaillardin and tetrahydrogaillardin, respectively; compounds III and IV have been obtained and characterized for the first time.



III R=OH
IV R=O

A mixture of our lactone with gaillardin gave no depression of the melting point.

The sample of gaillardin was kindly given to us by Prof. Morris Kupchan.

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A CRYSTALLINE SUBSTANCE FROM ARTEMISIA RUTIFOLIA

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From the green epigeal part of Artemisia rutifolia Steph. et Spreng. collected on August 5, 1967 in the flowering phase (Central Asia, region of the Turkestan range) we have isolated a colorless crystalline substance with the composition $C_{15}H_{18}O_5$, mp 235° C (decomp., from ethanol).

Chromatography in a thin layer of Al_2O_3 (activity grade IV) in the benzene–methanol (9 : 1) system gave a clear spot with R_f 0.55, revealed with a 1% solution of $KMnO_4$ in 1% H_2SO_4. IR spectrum, λ_{max}, cm^{-1}: 3520, 3580, 3620 (OH), 1765 (γ-lactone), 1660 and 820 (C=C). In the NMR spectrum there are two methyl singlets in the 1.23 and 1.63 ppm regions, two doublet at 5.39 and 6.0 ppm (J = 3 and 4 Hz) (an exocyclic methylene in conjugation with the carbonyl of a γ-lactone), and a quartet at 4.50 ppm (lactone proton).

The composition of the substance, its IR and NMR spectra, and its solubility on heating in alkalis shows that it is a sesquiterpene lactone.

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LACTONES FROM ARTEMISIA TENUISECTA

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The epigeal part (5 kg of leaves and flower heads) of Artemisia tenuisecta Nevski, collected in August 1968 in the Tashkent region, were extracted with chloroform. The concentrated extract was dissolved in 500 ml of ethanol, 400 ml of water was added, and the mixture was extracted with chloroform. The concentrated chloroform extract (25 g) was chromatographed on alumina (activity grade IV, 600 g). Elution with benzene gave a substance $C_{15}H_{18}O_3$, mp 168–170° C, identical with α-santonin [1].

Elution with benzene–methanol (19 : 1) gave a substance $C_{15}H_{22}O_4$ with mp 230–231° C; mol. wt. 266 (mass spectrometry); IR spectrum, cm^{-1}: 3470 (OH), 1750 (γ-lactone), 1650 and 810 (double bond). The NMR spectrum has a singlet at δ 0.82 ppm ($C-CH_3$, tertiary), a doublet at 1.20 ppm ($HC-CH_3$), and a singlet at 1.15 ppm [$C(OH)-CH_3$, tertiary]. The spectral characteristics show that the substance isolated is a sesquiterpene lactone of the type of selinane. Acetylation with acetic anhydride in pyridine gave an acetyl derivative $C_{17}H_{24}O_5$, mp 217–218° C. The IR spectrum of the latter retained the absorption band of a hydroxyl group. Consequently, the lactone is identical with mibulactone, as is shown by the results of a direct comparison of the IR spectra and by the melting point of a mixture of samples of these substances [2].