The IR spectrum and a mixed melting point confirmed the hypothesis that the substance isolated from D. coriacea and D. martiniciensis is rutin.

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2 June 1969 Leningrad Chemical and Pharmaceutical Institute

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# THE NATURE OF THE TERPENE ALCOHOL ACHILLENOL

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In a study of the composition of the essential oil of Achillea filipendulina (fernleaf yarrow) we isolated an alcohol $C_{10}H_{18}O$ with bp 83° C/20 mm, $d_{20}^{20}$ 0.8619, $n_D^{20}$ 1.4613; $[\alpha]_D^{20}$ +12.8°. It forms a colorless mobile liquid with the smell of mountain ash.

There is information [1] of the presence in this essential oil of an alcohol of this composition. Its properties differ from those of known terpene alcohols.

According to the IR spectrum, the alcohol is tertiary, since the absorption band due to the vibrations of the C—OH group is in the 1115–1185 $cm^{-1}$ region [2]. The presence of strong absorption bands at 915, 1003, 1636, and 3079 $cm^{-1}$ shows the presence of a vinyl group in the molecule. Medium-intensity bands at 633, 856, and 1672 $cm^{-1}$ apparently relate to the disubstituted −CH=CH− bond, which is confirmed by the Raman spectrum in the region of the frequencies of stretching vibrations of multiple bonds and the vibrations of hydrogen atoms (strong band at 1661 $cm^{-1}$ and a band at 3042 $cm^{-1}$ [3]). Thus, the alcohol under investigation is an aliphatic compound containing two multiple bonds.

A proof of this is the absorption of two molecules of hydrogen when the alcohol was hydrogenated in glacial acetic acid over $PtO_2$ according to Adams. This gave an aliphatic alcohol $C_{10}H_{22}O$ with $d_{20}^{20}$ 0.8436, $n_D^{20}$ 1.4403, $[\alpha]_D^{20}$ −7.2°.

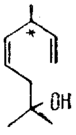
The most probable type of sketeton for the natural alcohol $C_{10}H_{18}O$ and the alcohol $C_{10}H_{22}O$ is that of 2, 6-dimethyloctane.

In alcohols with a skeleton of this type, the hydroxyl group may be present at $C_{(6)}$ or $C_{(2)}$. This choice was decided by the dehydration of the alcohol $C_{10}H_{22}O$ with thionyl chloride in pyridine, giving as the main product an optically active alcohol $C_{10}H_{20}$ with a methylene bond.

When the hydrocarbon $C_{10}H_{20}$ was hydrogenated by Adams' method, a saturated hydrocarbon $C_{10}H_{22}$, $d_{20}^{20}$ 0.7428, $n_D^{20}$ 1.4128, $[\alpha]_D^{20}$ +6.2°, was obtained which was similar to optically-inactive 2, 6-dimethyloctane [4].

To determine the position of the disubstituted multiple bond, which could be present either in either the 3-4 or the 4-5 position, we dehydrogenated the natural alcohol $C_{10}H_{18}O$ with thionyl chloride in pyridine. This gave a hydrocarbon with a third −C=CH double bond, $d_{20}^{20}$ 0.7836, $n_D^{20}$ 1.4526, $[\alpha]_D^{20}$ +64°. The electronic and IR spectra of the hydrocarbon showed the absence of conjugation between its multiple bonds, which is possible if the hydrocarbon possesses structure I. Therefore the alcohol isolated must have the structure of 2, 6-dimethylocta-4, 7-dien-2-ol (II). We have called this new natural alcohol achillenol.

I



II

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12 May 1968 Institute of Chemical Sciences, AS KazSSR

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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, $\nu_{max}$, $cm^{-1}$: 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); $\nu_{max}$, $cm^{-1}$: 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); $\nu_{max}$, $cm^{-1}$: 3480 (OH), 1768 (γ-lactone).

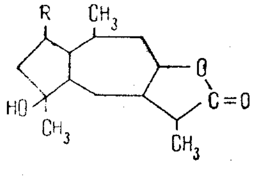
The oxidation of III with chromic anhydride in 90% acetic acid at 5° C for a day gave the desacetyldehydrotetrahydro derivative IV, $C_{15}H_{22}O_4$, with mp 196.5–199° C (from benzene); $\nu_{max}$, $cm^{-1}$: 3560 (OH), 1765 (γ-lactone), 1750 (cyclopentanone).

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.