protons of an exocyclic methylene group which can be present only in the C_4-C_{14} position since at the $C_{11}-C_{13}$ position these signals would be shifted to the low field by approximately 1 ppm [2]. The lactone proton appears in the form of a doublet at 4.30 ppm, which shows that it is located at C_5-C_6. A quartet in the 4.21 ppm region (J = 5 and 11 Hz) is due to a proton present in the geminal position to the OH group, i.e., artemin contains one secondary hydroxyl, which agrees with the results of acetylation.

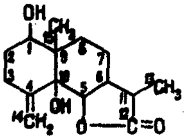
The NMR spectrum of the acetyl derivative retains the signals of quaternary and tertiary methyls (singlets at 0.98 ppm and doublet at 1.23 ppm), of the exocyclic methylene group (broadened signals in the 5.01 and 5.06 regions), and of the lactone proton (doublet at 4.27 ppm); the signal of an acetyl group appears (singlet at 2.01 ppm) and the signal of its geminal proton, as was to be expected, is displaced in the weak field direction (quartet at 5.41 ppm).

In the dihydro derivative, the signals of the exocyclic protons have disappeared; in place of them a new doublet has appeared in the 0.97 ppm region.

Three positions are possible for the tertiary hydroxyl: at C_{10}, C_{11}, and C_6. The position at C_{11} is excluded because in the NMR spectrum the CH_3 group appears in the form of a doublet, and of the remaining two possible positions the less likely is that at C_{10}, which agrees with the NMR spectrum of artemin. While the chemical shift between the H_6 and H_{11} protons will be comparatively large or the proton at C_6 will be absent, the signal from CH_3 at C_{11} must appear in the form of a well-defined doublet; in artemin and its derivatives the trough between the lines of the methyl doublet approaches half the height of the signal, which is connected with the combination lines arising from the interaction of the methyl proton at C_{11} with the proton on the neighboring carbon atom.

Several positions are possible for the secondary hydroxyl. We give our preference to the position at C_1 because the signal of the angular methyl group in the oxidized product—dehydroartemin—is shifted to the weak field, as we have also observed in the NMR spectra of tauremisin and taurin. On the basis of the biogenesis of the sesquiterpene lactones, we consider that the position of the OH group at C_8 is unlikely.

Thus, structure (I) is the most likely for artemin.



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AMBROSIN—A SESQUITERPENE LACTONE FROM *CYCLACHAENA XANTHIFOLIA*

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From the total sesquiterpene lactones of *C. xanthifolia* Fresen, family Compositae (rag sumpweed), we have obtained (yield 0.15%), by fractional crystallization from benzene, a substance $C_{15}H_{18}O_3$, chromatographically homogeneous on a thin layer of alumina [R_f 0.63, carbon tetrachloride—chloroform—ethanol (10 : 30 : 1)] and silica gel G [R_f 0.80, benzene—acetone (4 : 1)]; mp 144–146° C (from benzene); $[\alpha]_D^{20}$ −122° (c 8.7; chloroform). The IR spectrum (UR-10, KBr) exhibited absorption bands at 1760 (γ-lactone), 1640, 820 ($>C=CH_2$), 1710, 1585, and 1406 cm^{-1} (CO group of a five-membered ketone in conjugation with a double bond) [1]. The conjugation of the ketonic carbonyl with a double bond is also shown [2] by the characteristic absorption in the UV spectrum: λ_{max} (in ethanol) 219, 320 mμ (log ε 4.18; 1.70).

The properties of the substance obtained are similar to those given in the literature for the sesquiterpene lactone ambrosin.

With 2,4-dinitrophenylhydrazine in ethanol, we obtained ambrosin hydrazone with mp 87–89° C, confirming the presence of a keto group in the molecule.

When the substance was dissolved in aqueous alkalies, one mole of caustic soda was absorbed, which shows the presence in it of one saponifiable grouping, which may be a γ-lactone grouping [5]. The substance was brominated with $C_5H_5N \cdot HBr \cdot Br_2$ in chloroform. The crystalline bromination product had mp 142–144° C (from ether).

Oxidation of the substance with potassium permanganate in dry acetone yielded an acid with mp 128–130° C (from ether).

Hydrogenation of the substance in ethanol in the presence of palladized carbon formed a dihydro derivative $C_{15}H_{20}O_3$, mp 164–166° C (from ether), the IR spectrum of which did not have an absorption band at 1585 cm^{-1}. The UV spectrum exhibited the following maxima: 270 and 290 mμ (log ε 4.15 and 1.47), which are characteristic for a lactone carbonyl of a ketone group.

From what has been said it follows that the keto lactone obtained from the racemes of C. xanthifolia is identical with the sesquiterpene lactone ambrosin.

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INULICIN — A NEW SESQUITERPENE LACTONE FROM INULA JAPONICA

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From the epigeal part of Inula japonica Thunb family Compositae (Japan inula), collected on 22 August 1967 in the flowering phase, we have isolated a new sesquiterpene lactone—inulicin, $C_{17}H_{24}O_5$, with mp 125.5–126.5° C (from ethanol); $[\alpha]_D^{20}$ + 90.11° (c 4.69; chloroform).

The IR spectrum of the substance has absorption bands at 3502 cm^{-1} (OH) and 1745, 1660, and 1260 cm^{-1} (α-methylene-γ-lactone and $OCOCH_3$).

The NMR spectrum of inulicin has the signals of $CH_3{-}CH{-}$ (doublet, 1.05 ppm, J = 7 Hz), $CH_3{-}C{=}C{-}$ (singlet, 1.75 ppm), and $OCOCH_3$ groups (singlet 2.04 ppm), a $CH_2{=}C$ group in conjugation with a lactone carbonyl (doublets at 6.28 ppm, J = 2.9 Hz, and at 5.73 ppm, J = 2.8 Hz), of a proton present in the geminal position to an OH group (doublet, 4.29 ppm, J = 2.5 Hz), and of a vinyl proton (multiplet, 5.05 ppm). In the 3.9–4.05 ppm region there is a signal which can be ascribed to a lactone proton and a proton present in the geminal position to $OCOCH_3$.

Inulicin forms an acetyl derivative $C_{19}H_{26}O_6$ with mp 83.5–85.5° C (from ethanol; ν_{max} 1760 and 1665 cm^{-1} (α-methylene-γ-lactone ring), 1270 and 1730, 1230 cm^{-1} ($OCOCH_3$ group).

When inulicin was hydrogenated in ethanol in the presence of a small amount of Pt catalyst (Adams), a dihydro derivative $C_{17}H_{26}O_5$ was obtained with mp 56–58.5° C (from petroleum ether); ν_{max} 3510 (OH), 1750–1740, and 1260 cm^{-1} (γ-lactone and $OCOCH_3$); the signals of the exocyclic $CH_2{=}C$ group had disappeared from the NMR spectrum