STRUCTURE OF URSINOIC ACID AND URSININ

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Previously [1], one of us reported the isolation of two substances from the roots of Angelica ursina Rupr. et Schmalh., an oxocarboxylic acid with the composition $C_{15}H_{16}O_5$, anda substance with lactone properties, $C_{16}H_{20}O_7$, which we called, respectively, "ursinoic acid" and "ursinin." Continuing our study of these substances, we have directed our attention to the similarity of their UV spectra. The presence of an aromatic nucleus and a carbonyl group, and strong maxima in the 274- and 355-mμ region (log ε 4.27, 3.74) and at 280 and 335 (inflection) mμ (log ε 4.15 and 3.48), respectively, showed that these substances belonged to a single group of compounds based on a chromophore of the type Alk—O—Ar—CO. In this paper we give the results of a spectral study of these compounds.

In the IR spectrum (Fig. 1) of ursinoic acid $C_{15}H_{16}O_5$ (I) there are absorption bands at (cm^{-1}) 3200, 2600–2400, and 1740 (carboxyl group), 1675 (carbonyl group), 1630, 1590, and 1485 (aromatic nucleus), 1355 and 1380 (gem-dimethyl group), 900 (dimethylchromene ring), and 825 and 840 (1, 2, 3, 4-tetrasubstituted benzene nucleus). The presence of a carbonyl group was confirmed by the preparation of a 2, 4-dinitrophenylhydrazone with mp 234–235° C and the presence of a carboxyl group by the formation of a silver salt with mp 176–178° C (decomp).

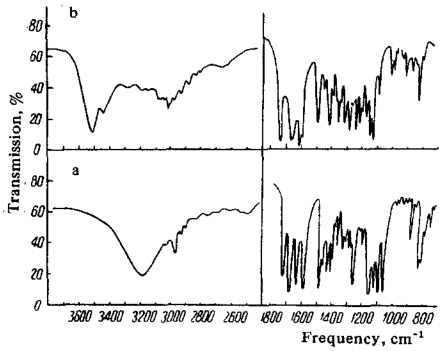
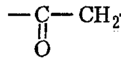


Fig. 1. IR spectra of a) ursinoic acid and b) ursinin.

In the NMR spectrum (Fig. 2) the signals of a dimethylchromene ring condensed with a benzene nucleus are observed: the singlet g at 1.41 ppm (6 H), the doublets *a* and b at 5.93 and 7.07 ppm, J = 12 Hz, due, respectively, to a gem-dimethyl group and to olefinic protons, and also two doublets c and d at 6.48 and 7.91 ppm, J = 8.5 Hz, due to two aromatic protons, one of which (c) is subject to the electron-donating influence of a OCH_3 group while the second (d) undergoes the magnetically anisotropic and electron-accepting influence of a C=O group. In addition to this, the section includes the signals of methylene protons in  $—\underset{\underset{O}{\|}}{C}—CH_2—COOH$ [singlet *f*, 2.66 ppm (2H)] and of a methoxyl group on an aromatic nucleus [singlet e, 3.88 ppm (3H)]. In the weak-field region there is a broad signal at 9.16 ppm due to the proton of a carboxyl group.

On the basis of what has been said, and also from biogenetic considerations, ursinoic acid may be ascribed structure I or II.

The signal d in the spectrum of I (see Fig. 2a) is shifted downfield (δ 7.91 ppm) compared with the signal of unsubstituted benzene, obviously because of the electron-accepting and anisotropic influence of the carbonyl group of the side chain. This favors structure I.

Ursinin (IV) has mol wt 306 (mass spectrometry) which, in agreement with previous results, shows the presence of 1 mole of water of crystallization, $C_{16}H_{18}O_6 \cdot H_2O$.

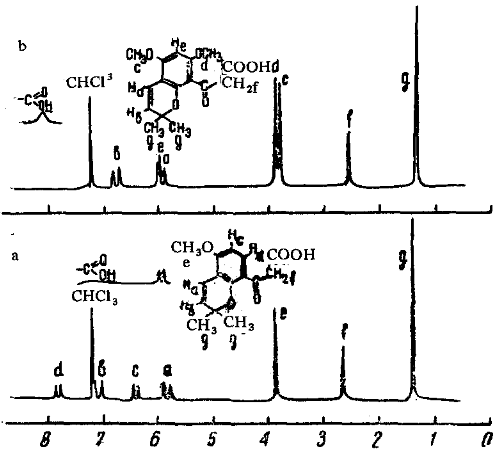
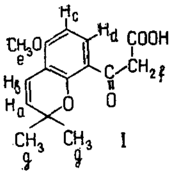
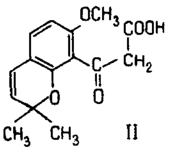
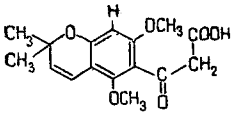
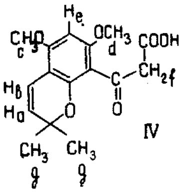


Fig. 2. NMR spectra of a) ursinoic acid and b) ursinin.


I


II


III


IV

When the substance was subjected to prolonged drying over phosphorous pentoxide in vacuo, the anhydrous form was obtained with 159–161° C. In the IR spectrum of the dried substance the band at 3500 cm^{-1} disappeared, the absorption at 1720 and 1650 cm^{-1} decreased considerably, and a strong broad band appeared at 1700 cm^{-1}. Absorption maxima at 870, 840, and 820 cm^{-1} show that the substance includes a 1, 2, 3, 4, 5-pentasubstituted benzene nucleus, that at 900 cm^{-1} shows a dimethylchromene ring, those at 1360 and 1385 cm^{-1} show a gem-dimethyl group, and those at 1260 and 1348 cm^{-1} show aryl methoxyl groups.

The UV spectrum taken in the presence of caustic alkali shows no bathochromic shift of the maximum, which indicates the absence of a free phenolic group. These facts lead to the conclusion that ursinin is an oxocarboxylic acid. This is confirmed, in particular, by the formation of a 2, 4-dinitrophenylhydrazone with mp 208–209° C and a silver salt with mp 260° C (decomp).

The NMR spectrum of ursinin (Fig. 2), like that of ursinoic acid, has the signals of the protons of a dimethylated chromene ring [two doublets *a* and b at 5.94 and 6.70 ppm, J = 12 Hz (1H each), and a singlet g at 1.34 ppm (6H), due, respectively, to olefinic protons and a gem-dimethyl group] and also the signal of the methylene protons in the $-\underset{\underset{O}{\|}}{C}-CH_2-COOH$ group [the singlet *f* at 2.55 ppm (2H)]. In the weak-field region there is a broad signal at 8.25 ppm (in the hydrate) and 10.48 ppm (in the anhydrous substance) relating to the proton of the carboxyl group. In addition to this, there are the signals of two methoxy groups attached to an aromatic nucleus, [singlets c and d, 3.78 and 3.85 ppm (3H each)] and that of a single aromatic proton [the singlet e, 5.97 ppm (1H)].

Thus, ursinin differs from ursinoic acid by the fact that one of the aromatic protons is replaced by a methoxyl group. On the basis of the facts given, ursinin may be ascribed structure III or IV.

We see from a comparison of the spectra I, III, and IV that the signals c (e) of an aromatic proton and b of an olefinic proton in III and IV undergo a diamagnetic shift of 0.51 and 0.37 ppm, respectively, compared with the analogous signals in I (see Figs. 2a and 2b). This is apparently due to the redistribution of the electron density over the carbon atoms in the ortho and para positions in the C=C—Ar system as a result of the additional electron-donating influence of the second OCH_3 group, which confirms the correctness of the choice of structures III and IV and excludes other variants.

In view of the simultaneous presence in one plant of two similar substances and the probable common nature of the mechanisms of their biosynthesis, it is logical to assume that ursinin is a methoxy derivative of ursinoic acid and has the structure IV.

The IR spectra were taken on a UR-10 spectrometer (KBr), and the NMR spectra on a JNM-4-H-100/100 MHz spectrometer (with HMDS as internal standard). The 2, 4-dinitrophenylhydrazones were obtained by a known method and the silver salts by the method described previously for ursinoic acid.

CONCLUSIONS

On the basis of UV, IR, and NMR spectroscopy, and the preparation of derivatives, the most probable structures of ursinoic acid and ursinin, aromatic oxo acids isolated previously from the roots of Angelica ursina Rupr. et Schmalh., have been established. It has been shown that the former has the structure 2', 2'-dimethylpyrano-5', 6': 5, 6-

(2, 4-dimethoxy)benzoylacetic acid while the second is 2', 2'-dimethylpyrano-5', 6': 5, 6-(2-methoxy)benzoylacetic acid.

REFERENCE

1. G. K. Nikonov and N. I. Rodina, ZhOKh, 33, 4012, 1963.

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