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Abstract

Full Text

CHEMISTRY

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THE STRUCTURE OF XANTHOGALOL AND ZOSIMOL

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Earlier ([1]) we reported the isolation from *Xanthogalum purpurascens* Lallem. of the coumarin xanthogalin, $C_{19}H_{20}O_5$, m.p. 100-102.5°, $[\alpha]_D^{16} = -41.4^\circ$ ($CHCl_3$). It was shown that the latter is an ester of the oxylactone xanthogalol, $C_{14}H_{14}O_4$, m.p. 183-185°, $[\alpha]_D^{16} = +13.7^\circ$ ($CHCl_3$), and angelic acid.

From another plant, *Zosimia absinthiifolia* (Vent) Link, an isomeric coumarin—zosimin—was isolated ([2]), m.p. 119-120°, $[\alpha]_D^{16} = +272^\circ$ ($CHCl_3$), likewise an ester and cleaved on saponification to the oxycoumarin zosimol, $C_{14}H_{14}O_4$, m.p. 156-158°, $[\alpha]_D^{22} = +209.4^\circ$ ($CHCl_3$), and tiglic acid.

Fig. 1. UV spectra in 96% ethanol of xanthogalol (solid curve) and zosimol (dashed)

In the present work the structure of xanthogalol and zosimol is considered. The UV spectra of both oxycoumarins (Fig. 1) are typical ([3,4]) of coumarin derivatives not condensed with other aromatic rings. The position and intensity of the absorption bands in the IR spectra (Fig. 2) confirm the presence of a coumarin skeleton (1710-1705, 1620-1610, and 1500-1495 cm^{-1}) and also indicate the absence of C—H bonds of a furan nucleus ([5,6]).

As was indicated in previous communications, the function of the fourth oxygen atom in xanthogalol and zosimol remained unclear. However, on the basis of the gross formula of both coumarins, the absence of carbonyl and methoxyl groups, and the presence in their IR spectra of C—O bond bands at the aromatic nucleus (1256 cm^{-1} for xanthogalol and 1265 cm^{-1} for zosimol), it may be assumed that the fourth oxygen atom is part of a nonaromatic ring.

In the NMR spectra of xanthogalin and zosimin (Fig. 3), in the low-field region (δ 6-8 ppm*) two quadruplets are visible. As was shown ([7,8]), doublets *a* and

Fig. 2. IR spectra in Vaseline oil of xanthogalol (a) and zosimol (b)

Figure 2: Fig. 2. IR spectra in Vaseline oil of xanthogalol (a) and zosimol (b)

Fig. 3. NMR spectra of xanthogalin (A), zosimin (B), deltoin (C) in CCl_4 and xanthogalol (D), zosimol (E), and marmesin (F) in $CHCl_3$

Figure 3: Fig. 3. NMR spectra of xanthogalin (A), zosimin (B), deltoin (C) in CCl_4 and xanthogalol (D), zosimol (E), and marmesin (F) in $CHCl_3$

d correspond to signals of protons in positions 4 and 3, while *b* and *c* are due to protons in positions 5 and 6. Thus, the compounds under investigation are 7,8-disubstituted coumarins.

In the NMR spectra of xanthogalol and zosimol, in the region from 1 to 6 ppm, there are 4 groups of lines, designated in Fig. 3 as *a*, *b*, *c*, and *d*. Triplet *a* (for xanthogalol $\delta = 3.89$, $J = 6$ Hz; for zosimol $\delta = 4.73$, $J = 8$ Hz) and doublet *b* (for xanthogalol a broad peak with indistinct splitting, $\delta = 3.02$; for zosimol $\delta = 3.26$, $J = 8$ Hz) correspond to the methine proton and to the protons of the adjacent methylene group, attached, in turn, to the aromatic ring. Singlet *c* is apparently due to the proton of the hydroxyl.

* Chemical shifts were measured in millionths relative to tetramethylsilane as an internal standard, taken as 0.

Finally, two *d* peaks ($\delta = 1.31$ and 1.36 for xanthogalol and $\delta = 1.21$ and 1.31 for zosimol) correspond to two nonequivalent aliphatic methyl groups. This assignment is also fully confirmed by the ratio of the integrated intensities of the signals $a : b : c : d$, $1 : 2 : 1 : 6$.

Thus, the nature of all the protons present in the molecule is determined.

Fig. 2. IR spectra in Vaseline oil of xanthogalol (**a**) and zosimol (**b**)

Fig. 3. NMR spectra of xanthogalin (**A**), zosimin ( ), deltoin ( ) in CCl_4 and xanthogalol ( ), zosimol ( ), and marmesin ( ) in $CHCl_3$

On the basis of the foregoing, and also taking into account that natural coumarins are derivatives of umbelliferone (7-hydroxycoumarin), xanthogalol and zosimol may each be assigned one of the following structures:

(I) (II)

The choice between these formulas can be made on the basis of the following considerations.

In structure (II), the methine proton is adjacent to an oxygen atom having a reduced electron density as a result of conjugation with the carbonyl group of the α-pyrone ring. The electron-acceptor influence of oxygen in this case will

structural formulas III, IV, and V

Figure 4: structural formulas III, IV, and V

be greater than that of the oxygen atom of the hydroxyl group (in structure I), owing to which the shielding of the methine proton will decrease and its signal should lie in a region of weaker field. On the other hand, for the same reason the signals of the methyl groups for structure II should be located in a region of stronger field in comparison with structure I, although this shift should be smaller than for the methine, since the influence of the oxygen on the latter is transmitted through only two bonds, whereas for the protons of the methyls it is transmitted through three bonds.

The data obtained show that in the spectrum of zosimol the signal of the methine proton is observed in a weaker field ($\delta = 4.73$) compared with xanthogalol ($\delta = 3.89$), while the signals of the methyl groups ($\delta = 1.21$ and 1.31), on the contrary, are in a somewhat stronger field (for xanthogalol $\delta = 1.31$ and 1.36). In accordance with this, formula I should be assigned to xanthogalol, and formula II to zosimol.

The conclusion reached is also confirmed by the practical identity of the NMR spectral region of zosimol and marmesin [⁀9] (III) due to aliphatic protons. According to the ideas set forth above, these two compounds differ only in the point of attachment of the dihydrofuran ring to coumarin.

(III) (IV) (V)

In addition, in the NMR spectra of their ethers—zosimine (IV) and deltoin [⁀10] (V)—one and the same shift of the signals of the aliphatic methyl groups into the weak-field region (by 0.3 ppm) is observed; these signals merge with the signals of the olefinic methyl groups of tiglic and angelic acids. This is explained by additional deshielding of the methyls by the ester group. Such an explanation is confirmed by an analogous shift of the peaks of the methyl protons in marmesin acetate as compared with marmesin ($\Delta\delta = 0.25$ ppm). In the ether of xanthogalol—xanthogalin (VI)—no similar phenomenon is observed, since the methyl groups in this compound are one bond farther away from the corresponding electron-acceptor grouping. In this case, however, the ester group exerts a deshielding effect on the methine proton, the signal of which is shifted into the weak-field region by 1.24 ppm.

The nonequivalence of the methyl groups in zosimol is apparently associated with fixation of the spatial position of the $(CH_3)_2C(OH)$ group relative to the rest of the molecule. This fixation is possibly due to the formation of an intramolecular hydrogen bond between the hydroxyl group and the oxygen of the dihydrofuran ring. A similar phenomenon is observed in the NMR spectrum of marmesin. In the case of xanthogalol, rotation of the $C(CH_3)_2$ group cannot occur at all, and the two methyls are shielded differently owing to the cis- and trans-arrangement relative to the hydroxyl. This, evidently, also accounts for

the nonequivalence of the methy-

···of the tiglinoyl group, as a result of which in the spectrum of xanthogalol, instead of a sharp doublet, a broad peak is present.

The data on the structure of zozimol were also partially confirmed by obtaining, upon its dehydration with phosphorus pentoxide, a compound $C_{14}H_{12}O_3$, m.p. 139°, whose constants corresponded to the literature data ([11]) for dihydrooroselone (VII).

[structural formula of compound (VI)] [structural formula of compound (VII)]

IR spectra were obtained on a UR-10 spectrophotometer, UV spectra on an SF-4 spectrophotometer, and NMR spectra were recorded on a JNM-C-60 NMR spectrometer (60 MHz).

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Note: Figure translations are in progress. See original paper for figures.