# SOME FEATURES OF THE IR SPECTRA OF ISOCOUMARINS

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It is known that in the IR spectra of the isocoumarins, the absorption bands of the carbonyl group in the 1672-1730 cm$^{-1}$ range lie below the bands of aromatic $\gamma$-lactones (1748-1770 cm$^{-1}$) and of saturated $\delta$-lactones (1740 cm$^{-1}$) [1]. In synthetic isocoumarin derivatives, electron-accepting substituents (Ar, $-COOC_2H_5$, $-CN$) in positions 3 and 4 cause a shift in the absorption bands both of the carbonyl group and of the double bond of the $\alpha$-pyrone ring. In this case, the frequency of the carbonyl group may be raised to 1750 cm$^{-1}$ and the absorption band of the double bond of the lactone ring be shifted from 1660 to 1615 cm$^{-1}$ [2].

However, an intense carbonyl group absorption band in the 1650-1755 cm$^{-1}$ region may belong not only to an isocoumarin but also to a chromone (1630-1690 cm$^{-1}$) [3, 4], to a coumarin, or to a furocoumarin [5, 6]. Consequently, the identification of a substance as an isocoumarin cannot be performed reliably only from the region of the carbonyl absorption band.

In a comparative study of the IR spectra of artemidin, artemidinal, and their derivatives [7, 8], and of capillarin [9] and other isocoumarins [10-13], we have observed their similarity in the 1550-1755 cm$^{-1}$ region. In the range considered, four absorption bands appear with a characteristic intensity ratio. The strongest of them is the carbonyl band of the lactone ring (1670-1755 cm$^{-1}$), followed by the absorption band of the double bond in the 3,4 position (1615-1660 cm$^{-1}$), the band at 1590-1625 cm$^{-1}$, and the smallest peak at 1550-1590 cm$^{-1}$, belonging to the aromatic ring (Fig. 1). An increase in the intensity of the 1622 cm$^{-1}$ band in artemidin is due to the superposition in this region of the band of the conjugated double bond of the side chain at $C_3$, and the disturbance of the sequence of the bands in artemidinal is due to the influence of the second carbonyl group at $C_3$.

When a hydroxyl is present in position 8 of the isocoumarins, a strong intramolecular hydrogen bond is formed between the hydroxy and the carbonyl groups, whereupon the frequencies of the carbonyl and of the double bond of the vinyl group fall to 1670 and 1645 cm$^{-1}$, respectively.

Where the hydroxy group at $C_8$ is etherified or esterified, dissimilar increases in the frequency of the carbonyl group absorption are observed. For example, 8-methoxy-3-methylisocoumarin has the maximum at 1727 cm$^{-1}$ and 8-acetoxy-3,4-dimethylisocoumarin has it at 1710 cm$^{-1}$. These differences in frequency depend on the substituents in position 8.

For the dihydroisocoumarins considered, three absorption bands are found in the 1500-1720 cm$^{-1}$ region with maxima at 1670-1720 cm$^{-1}$ (C=O) and at 1620 and 1580 cm$^{-1}$ (aromatic ring).

## SUMMARY

It has been established that in the IR spectra of isocoumarin compounds four absorption bands with a characteristic intensity ratio appear in the 1550-1755 cm$^{-1}$ region. This makes it possible to determine whether a natural substance is an isocoumarin compound.

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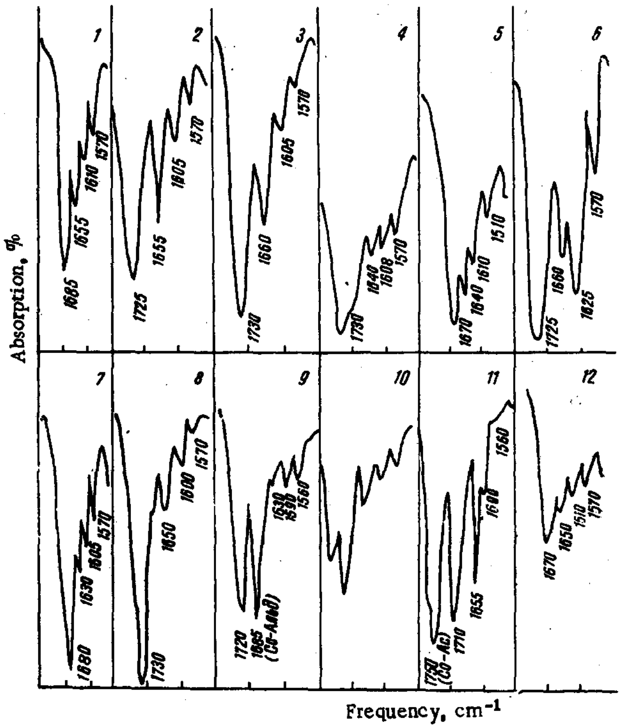

Fig. 1. IR spectra of 8-hydroxy-3-methylisocoumarin (1), 3-(but-2-ynyl)isocoumarin (capillarin) (2), 3-butylisocoumarin (dihydroartemidin) (3), methyl isocoumarin-3-carboxylate (4), 4-(1,2-dihydroxyethyl)-8-hydroxyisocoumarin (oospoglycol) (5), 3-(but-1-enyl)isocoumarin (artemidin) (6), 8-hydroxyisocoumarin-4-carboxylic acid (oospoic acid) (7), 3-(1,2-dibromobutyl)isocoumarin (dibromoartemidin) (8), isocoumarin-3-carbaldehyde (artemidinal) (9), 8-acetoxy-3,4-dimethylisocoumarin (acetyloospolactone) (10), 4-(2-acetoglycol)-8-acetoxyisocoumarin (diacetyloosponol) (11), 8-hydroxy-3,4-dimethylisocoumarin (oospolactone) (12).

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