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INTEGRAL INTENSITIES OF THE ABSORPTION BANDS OF THE SKELETAL VIBRATIONS OF SUBSTITUTED FUROCOUMARINS

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An analysis of the IR spectra of coumarins and furocoumarins permits their rapid identification and the solution of many questions connected with the chemical structure of these compounds [1-8].

Previously, one of us [5] expressed the opinion that it is possible to distinguish coumarins from furocoumarins and dihydrofurocoumarins from the intensity of the absorption bands of the C=C bonds at 1630-1650 cm^{-1}. In addition, it is possible to distinguish 5- and 8-substituted furocoumarins from the intensity of the absorption bands in this range of frequencies. This idea has been used successfully in determining the structure of new natural coumarins [5,9].

To confirm this idea, we have used the integral intensity of the absorption bands of the C=C bonds in the spectral region of 1630-1560 cm^{-1} for the 5- and 8-hydroxyfurocoumarins and their esters and for the 4',5'-dihydrofurocoumarins (table).

The absorption bands of the stretching vibrations of the C=C bonds of the furan, pyrone, and aromatic rings appear in the region of the spectrum considered (figure). The stretching vibrations of the C=C bonds of the first two systems give an absorption band at 1630-1605 cm^{-1}. An absorption band at 1575-1585 cm^{-1} is due to the stretching vibrations of the carbon-carbon bonds of the aromatic ring, while 5-substituted furocoumarins have two strong absorption bands in the 1625-1605 and 1580-1575 cm^{-1} regions. The first of them is sometimes split into two bands of approximately equal intensities*. In addition, in the spectra of these derivatives an absorption band appears distinctly at 1550 cm^{-1}. Furocoumarins substituted in position 8 give two absorption bands of markedly different intensities at 1620 and 1585 cm^{-1}.

For substituted benzene, and also for furocoumarins substituted in position 5 (or 8) or 5 and 8, i.e., in the aromatic ring, the intensities and number of the bands are considerably more important than their frequencies [11]. In the determination of the structure of new coumarin and furocoumarin derivatives, the consideration of these features of their IR spectra plays a particularly important part.

It can be seen from the table that the intensities of the absorption bands at 1630-1600 and 1575 cm^{-1} are different where OH, methoxyl, and alkoxyl groups are found in position 5 or 8 of the benzene ring of a furocoumarin. The integral intensity of the absorption band at 1630-1620 cm^{-1} in the IR spectra of the 8-substituted furocoumarins (1–4) is lower than for the furocoumarins substituted in position 5 (5–10). At the same time, the integral intensity of the absorption band at 1585 cm^{-1} in the former compounds is higher than in the 5-substituted furocoumarins, with the exception of isoimperatorin.

A complication of the structure of the substituent and the appearance of a double bond, an oxide ring, or hydroxyl groups leads to an increase in the integral intensities of the given bands (see table). 4',5'-Dihydrofurocoumarins—for example, marmesin and its esters—give two strong absorption bands in the 1650-1500 cm^{-1} region of the spectrum. In this case, the absorption band at 1625 cm^{-1} is not split into two, as in the 5-substituted furocoumarins.

In addition to IR spectroscopy, UV spectroscopy is very important in the study of the natural coumarin. One of us has pointed out previously [12] that it is possible to distinguish furocoumarins from coumarins and dihydrofurocoumarins, and 5-substituted furocoumarins from the 8-substituted compounds, by the nature of the absorption in the ultraviolet region [5,6,9].

Conclusions

The IR spectra of 5- and 8-hydroxyfurocoumarins and their esters, 5,8-disubstituted furocoumarins containing hydroxyl, methoxyl, and alkoxyl groups, and 4',5'-dihydrofurocoumarins differ with respect to the intensity and number of the bands in the 1630-1500 cm^{-1} region of the spectrum. The integral intensities of the absorption bands in this frequency region differ markedly in the derivatives mentioned.

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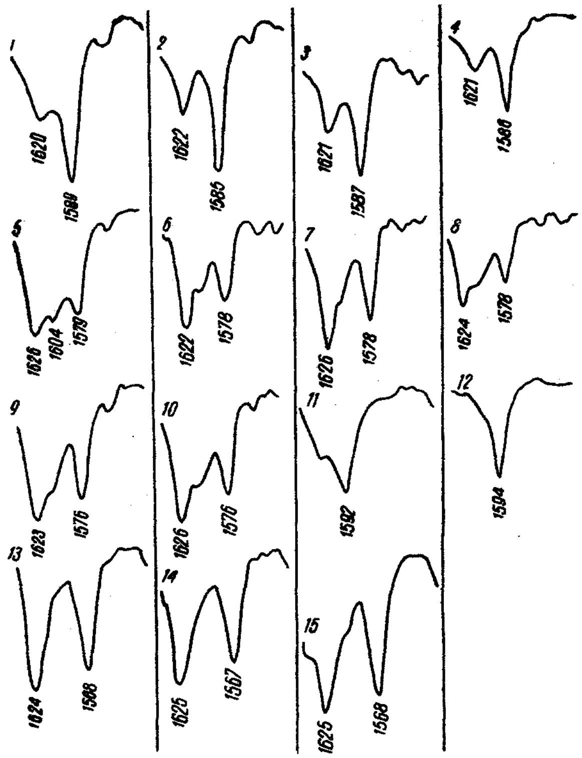
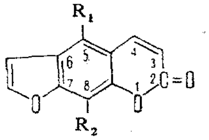
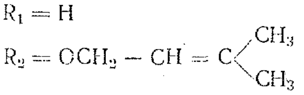
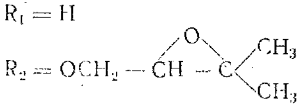
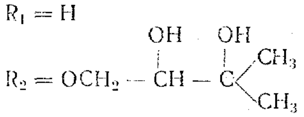
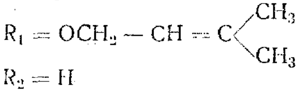
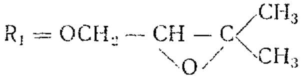
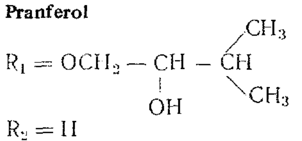
*Splitting is observed when the spectra are recorded of the substances in the form of mulls in paraffin oil; in solution in chloroform the splitting disappears and a small shoulder is found.

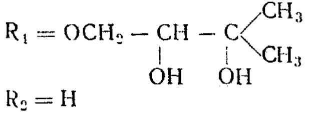
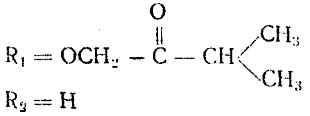
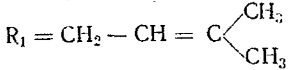
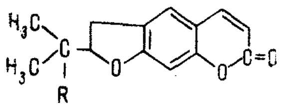
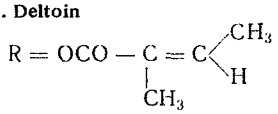
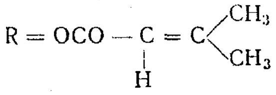


IR spectra of xanthotoxin (1), imperatorin (2), prangenin (3), pragenin hydrate (4), bergapten (5), isoimperator (6), oxypeucedanin (7), pranferol (8), oxypeucedanin (9), isooxypeucedanin (10), isopimpinellin (11), alloimperatorin (12), marmesin (13), deltoin (14), and pranchimgin (15).

Integral Intensities of the Absorption Bands of the Skeletal Vibrations of Substituted Furocoumarins*

Compound	Frequency of the C=C bond, cm^{-1}	Intensity of the band A · 10^{-4}, mole^{-1} · l · cm^{-1}
Furocoumarins substituted in position 8		
1. Xanthotoxin	1623	1,35
$R_1 = H$	1588	1.68
		
$R_2 = OCH_3$		
2. Imperatorin	1620	1.39
$R_1 = H$	1585	2.44
 $R_2 = OCH_2-CH=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$		
3. Prangenin	1622	1,34
$R_1 = H$	1587	2,72
 $R_2 = OCH_2-\underset{\;}{CH}\overset{O}{\frown}C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$		
4. Prangenin hydrate	1620	1.69
$R_1 = H$	1587	2,35
 $R_2 = OCH_2-\overset{OH}{\overset{\vert}{CH}}-\overset{OH}{\overset{\vert}{C}}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$		
Furocoumarins substituted position 5		
5. Bergapten	1620	4,90
$R_1 = OCH_3$		
$R_2 = H$	1580	1,41
6. Isoimperatorin	1622	3.79
 $R_1 = OCH_2-CH=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$		
$R_2 = H$	1577	1,95
7. Oxypeucedanin	1624	3.92
 $R_1 = OCH_2-CH\underset{O}{\smile}C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$		
$R_2 = H$	1578	1,53
8. Pranferol	1624	3.60
 $R_1 = OCH_2-\underset{OH}{\underset{\vert}{CH}}-CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$		
$R_2 = H$	1578	1.54

Continuation of Table

Compound	Frequency of the C=C bond, cm^{-1}	Intensity of the band $A \cdot 10^{-4}$. $mole^{-1} \cdot l \cdot cm^{-1}$
9. **Oxypeucedanin hydrate**  $R_1 = OCH_2-\underset{OH}{\underset{\vert}{CH}}-\underset{OH}{\underset{\vert}{C}}\langle^{CH_3}_{CH_3}$	1623	3.67
$R_2 = H$	1576	1.49
10. **Isooxypeucedanin**  $R_1 = OCH_2-\overset{O}{\overset{\Vert}{C}}-CH\langle^{CH_3}_{CH_3}$	1625	3.84
$R_2 = H$	1575	1.28
5,8-Disubstituted furocoumarins		
11. **Isopimpinellin** $R_1 = R_2 = OCH_3$	1622 1590	1.48 3.56
12. **Alloimperatorin**  $R_1 = CH_2-CH=C\langle^{CH_3}_{CH_3}$	1607	1.72
$R_2 = OH$	1593	2.18
4,5'-Dihydrofurocoumarins		
13. **Marmesin** 	1624	4.15
$R = OH$	1568	2.32
14. **Deltoin**  $R = OCO-\underset{CH_3}{\underset{\vert}{C}}=C\langle^{CH_3}_{H}$	1625	5.14
	1568	2.85
15. **Pranchimgin**  $R = OCO-\underset{H}{\underset{\vert}{C}}=C\langle^{CH_3}_{CH_3}$	1625	6.28
	1559	2.60

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*The IR spectra were recorded on a UR-10 spectrophotometer. Chloroform was used as solvent. The calculation of the integral intensity of the absorption bands was carried out by Burgin's method taking the correction for the "wing" into account [10].

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