ANALYSIS OF THE CHARACTERISTIC ABSORPTION BANDS OF THE STRETCHING VIBRATIONS OF THE LACTONE CARBONYL GROUPS IN IR SPECTRA OF NATURAL PSEUDOGUAIANOLIDES

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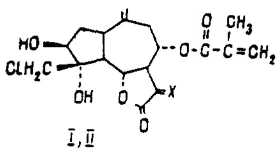
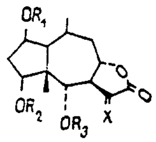
We have shown previously [1] that the change in IR-spectral characteristics (frequency and integral intensity) of the absorption band of the stretching vibrations of the lactone carbonyl groups of natural guaianolides is due to a change in the internal strain of the 6,7-linked γ-lactone rings.

We have now studied the integral intensities and frequencies of the IR absorption bands of the stretching vibrations of the lactone carbonyls of natural pseudoguaianolides with the 7,8-linkage of the γ-lactone ring. Below are given the results for two guaianolides, (I), and (II), and seven pseudoguaianolides, five of which [(III)-(VII)] have α,β-unsaturated γ-lactone rings and two [(VIII) and (IX)] saturated γ-lactone rings (fragments):

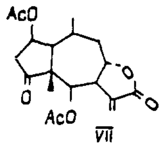
Compound		lactone $\nu_{C=O}$ cm^{-1}	$A_{C=O} \cdot 10^4$, liter mole$^{-1} \cdot$cm^{-1}	Literature
I.	Elegin	1765	5.00	3
II.	Dihydroelegin	1775	6.30	3
III.	Britannin	1770	4.63	4
IV.	Erigerolide	1760	4.40	4
V.	Ergolide	1765	4.70	5
VI.	Carpesiolide	1760	4.68	6
VII.	Dehydrobritannin	1760	4.80	4
VIII.	Dihydroergolide	1770	5.76	5
IX.	Dihydrobritannin	1775	5.98	4



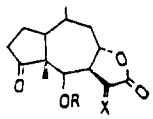
I, II



III, IV, IX



VII



V, VI, VII

I. X = CH_2
II. X = α-Me, H
III. R_1 = Ac; R_2 = H; R_3 = Ac; X = CH_2
IV. R_1 = Ac; R_2 = Ac; R_3 = H; X = CH_2
V. R = Ac. X = CH_2
VI. R = H; X = CH_2
VIII. R = Ac; X = α-Me, H
IX. R_1 = Ac; R_2 = Ac; R_3 = H; X = α-Me, H

From an analysis of the facts given above it follows that pseudoguaianolides containing α,β-unsaturated γ-lactone rings have frequencies and intensities of the absorption bands that are lower than those for dihydroergolide (VIII) and dihydrobritannin (IX).

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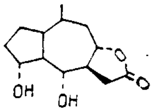
Thus, for example, britannin has the absorption maximum $\nu_{C=O}$ 1770 cm^{-1} and an integral intensity (A) of 4.63 practical units, while for dihydrobritannin the corresponding parameters are $\nu_{C=O}$ = 1775 cm^{-1} and $A_{C=O}$ = 5.98 practical units.

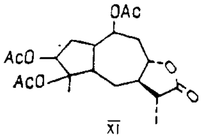
On the basis of the investigations performed of the IR spectral characteristics of natural guaianolides with 6,7-linked γ-lactone rings [1], the lowering of $A_{C=O}$ and $\nu_{C=O}$ in compounds [(III)-(VII)] as compared with dihydroergolide (VIII) and dihydrobritannin (IX) can be explained by the influence of Van der Waals forces of repulsion between the lactone carbonyl and the exomethylene group.

The increase in the values of $A_{C=O}$ and $\nu_{C=O}$ in dihydrobritannin and dihydroergolide, as also in the case of a 6,7-linked saturated lactone moiety [compound (II)] is due, in all probability, to angular strain of the cyclic system of the lactone ring.

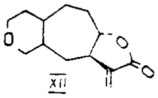
This conclusion is confirmed by the substantial difference in the torsional angles cd—bd (about 8°, according to x-ray structural results) of the lactone ring in 7,8-linked guaianolides [(X) and (XI)] relative to the sesquiterpene lactone (XII) [2, 7].



X



XI



XII

Thus, the IR-spectral results obtained for the absorption bands of the stretching vibrations of the lactone carbonyl show that pseudoguaianolides having 7,8-linked γ-lactone rings obey the laws established previously that were found for the 6,7-linked natural guaianolides.

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