8. N. P. Chernobrivkina and A. A. Stepanov, The Composition of the Essential Oil of Spruce and Pine Needles, Birch Buds, and Rhododendron Leaves. Lipid Metabolism of Woody Plants under the Conditions of the North [in Russian], KF AN SSSR, Petrozavodsk (1983), p. 132.
9. V. M. Vershnyak, Birch Saplings in Central Yakutia. Biological Resources of the Siberian Forests [in Russian], ILiD SO AN SSSR [Forest and Timber Institute of the Siberian Branch of the USSR Academy of Sciences], Krasnovarsk (1980), p. 106.

FREQUENCIES AND INTEGRAL INTENSITIES OF THE LACTONE AND ESTER CARBONYLS OF NATURAL GUAIANOLIDES

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The frequencies and integral intensities of the IR bands of the stretching vibrations of lactone and acyclic ester carbonyls at C-8 of ten natural guaianolides and their derivatives, and of three model compounds have been studied. The most probable interpretation of the change in the value of $A\nu_{C=O}$ and $\nu_{C=O}$ of the lactone carbonyl have been suggested. In elegin and some of its derivatives, acroptilin, chlorohyssopifolin B, and eleganin, a lowering of the values of $A\nu_{C=O}$ and $\nu_{C=O}$ in comparison with dihydroelegin, hexahydroelegin, and the hydroxylactone of cynaropicrin is caused by nonvalent interactions of the lactone carbonyl with the α-exocyclic double bond. The increase in $A\nu_{C=O}$ and $\nu_{C=O}$ in dihydroelegin, hexahydroelegen, and the hydroxylactone of cynaropicrin is due to the angular strain of the γ-lactone ring. It has been shown that in an acyclic side chain at C-8 an increase in the integral intensity and in the frequency of the α,β-unsaturated ester carbonyl relative to guaianolides in which the terminal vinyl group at C-17 is absent is due to a conjugation effect.

It is known that the frequencies of the absorption bands in IR spectra due to the stretching vibrations $\nu_{C=O}$ in lactones are characteristic, and there are, therefore, grounds for assuming that the integral intensities of these bands can serve as a criterion for evaluating electronic and stereochemical changes taking place in the lactone molecules. In contrast to coumarins, chromones, and xanthones [1], there is no analysis in the literature of the frequencies and, in particular, the integral intensities of $\nu_{C=O}$ of sesquiterpene lactones [2]. We have studied the frequencies and integral intensities of the IR bands in the 1600-1800 cm^{-1} region, which correspond to the stretching vibrations of a carbonyl group in a γ-lactone ring and of an ester carbonyl group in an acyclic side chain at C-8 of the guaianolide series.

Table 1 gives the frequencies and integral intensities of the absorption bands of the carbonyl groups in guaianolides (IV-XIII) investigated. Analysis of the figures in the Table leads to the following results. The integral intensity (A) of the IR band of the carbonyl group of the lactone ring of each of compounds (IV)-(X) with an exocyclic double bond at C-11 amounts to 4.60-5.00 practical units (10^4 liter·mole^{-1}·cm^{-2}), and the absorption frequency corresponding to it is 1765 ± 5 cm^{-1}.

In the case of an alkyl substituent in the α-position of the γ-lactone ring, as, for example, in hydrodroelegin (XI) and hexahydroelegin (XII), the value of $A\nu_{C=O}$ rises to 5.60-6.00 pr.u., and the value of $\nu_{C=O}$ shifts in the high frequency direction by 8-10 cm^{-1}.

On comparing the model compounds (I-III) it may be noted that the presence of α-exocyclic double bond in the cyclopentanone ring (compound (II)) considerably decreases the integral intensity ($A\nu_{C=O}$ = 1.75 pr.u.) and the frequency ($\nu_{C=O}$ = 1727 cm^{-1}) of the carbonyl group in comparison with cyclopentanone ($A\nu_{C=O}$ = 3.0 pr.u., $\nu_{C=O}$ = 1748 cm^{-1}).

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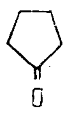
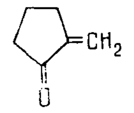
TABLE 1. Values of $A\nu_{C=O}$ and $\nu_{C=O}$ for the Absorption Bands of the Lactone and Ester Carbonyls of the Guaianolides Investigated



I



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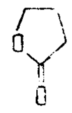

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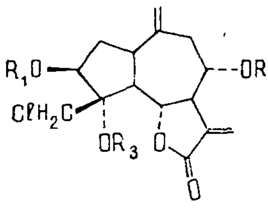
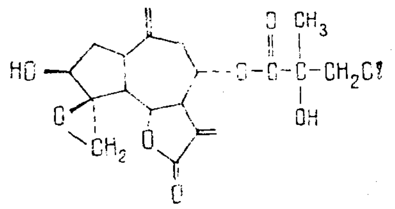


IV-VII, IX



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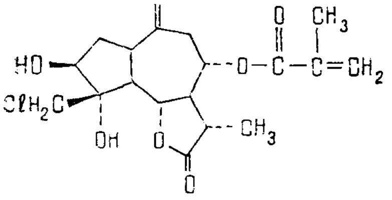
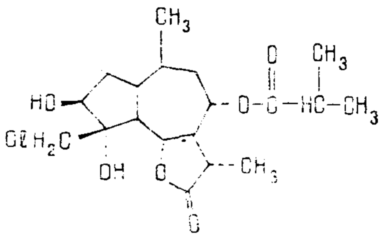
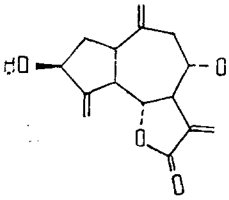


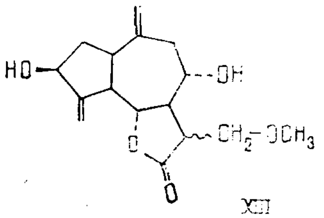
XI



XII



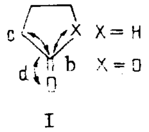
X



XIII

Compound	Lactone $\nu_{C=O}$ cm^{-1}	$A\nu_{C=O}\cdot 10^4$, liter·mole^{-1}·cm^{-1}	$\nu_{O-C=O}$ at C_8, cm^{-1}	$A_1\cdot 10^4$ liter·mole^{-1}·cm^{-1}	Literature
I. Cyclopentanone	1743	3,00	—	—	11
II. 2-Isopropylidenecyclopentanone	1727	1,75	—	—	11
III. γ-Butyrolactone	1770	5,90	—	—	
IV. Elegin $R_1 = R_3 = H;\ R_2 = -\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{\mid}}{C}=CH_2$	1765	5,00	1710	4,0	
V. Chlorohyssopifolin A (hyrcanin) $R_1 = R_3 = H;\ R_2 = -\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-CH_2Cl$	1763	4,60	1745	3,0	
VI. Elegin monoacetate $R_1 = Ac;\ R_2 = -\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{\mid}}{C}=CH_2;\ R_3 = H$	1760 1740 1710	9,80			
VII. Elegin diacetate $R_1 = Ac;\ R_2 = -\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{\mid}}{C}=CH_2;\ R_3 = Ac$	1760 1740 1710	11,70			
VIII. Acroptilin	1765	5,0	1745	3,20	
IX. Chlorohyssopifolin $R_1 = R_2 = R_3 = H$	1765	4,88			
X. Eleganin	1765	5,30	—	—	
XI. Dihydroelegin	1775	6,30	1710	3,63	
XII. Hexahydroelegin	1773	5,65	1725	3,40	
XIII. Hydroxylacetone of cynaropicrin	1773	5,60	—	—	

TABLE 2. Valence Angles of Cyclopentanone, γ-Butyrolactone, and Some Guaianolides, deg



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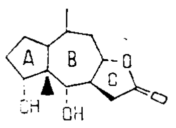
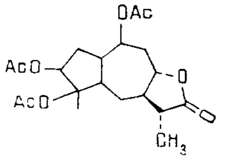
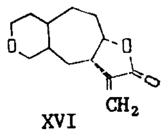


XIV



XV



XVI

Compound	*bc*	*bd*	*cd*	*cd−bd*	*d*	Literature source
I. Cyclopentanone	110,6	124.7	124,7	0	1,27	18
II. γ-Butyrolactone	109,7	121.7	127.6	6,9	1.19	19
XIV. (±)-4,5-Dihydroxy-4a,8-dimethylazuleno[6,5-a]furan-2(3H)-one	109.8	121,1	120,1	8	1,20	19
XI. Hymenolane	110 0	121.6	128.6	7	1,20	20
XVI. Hymenoxone	109,7	122,4	127,8	4,6	1,22	20

On the introduction of an oxygen heteroatom into the α-position of the cyclopentanone ring (III), the integral intensity and the frequency of the absorption band of the γ-lactone carbonyl increase considerably ($A\nu_{C=O}$ = 5.90 pr.u., $\nu_{C=O}$ = 1770 cm^{-1}).

These experimental facts characterizing the changes in $A\nu_{C=O}$ and $\nu_{C=O}$ in the model compounds (I-III) and in the γ-lactone rings of quaianolides (IV-X) relative to the guaianolides (X-XIII) exclude a mesomeric interaction between the carbonyl of the lactone ring and the α-exocyclic double bond and also an electrostatic interaction of these groups through space (field effect) [2]. As has been established for a large number of coumarins, chromenes, and xanthones [1], α,β-unsaturated ketones [3, 4], and vinyl esters [5], the conjugation effect causes a rise in $A\nu_{C=O}$ and a fall in the frequency $\nu_{C=O}$.

It has been found that in the case of the dominating influence of the field effect the IR-spectral parameters of the carbonyl absorption band change in the reverse order. As an example we can give α-pyrones with acceptor substituents (NO_2, SO_2Cl) in position 3 [1].

Furthermore, it has been established that in cyclic ketones and esters the values of $A\nu_{C=O}$ and $\nu_{C=O}$ decrease with an increase in the size of the ring [6, 7]. It is considered that this change in the IR-spectral parameters of carbonyl absorption is due to a change in the internal strain of the system, which includes angular Pitzer strains and van der Waals repulsive forces [7-9]. In rings with the same number of carbon atoms, the contribution of each of these types of strains depends on the nature of the ring (ketone or lactone) and also on the electron donor or acceptor properties of substituents and their position in the ring [10].

A study of the stereochemistry of α,β-unsaturated cis-stabilized ketones [11] and a consideration of a Dreiding model showed the noncoplanarity of the >C=O and >C=CH$_2$ substituents in 2-isopropylidenecyclopentanone ((II), (Table 1)).

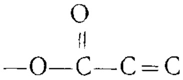
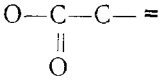
On this basis, it may be assumed that a lowering of the values of $A\nu_{C=O}$ and $\nu_{C=O}$ for compound (II) (see Table 1), relative to the spectral parameters for cyclopentanone (I) (Table 1), is caused by the van der Waals repulsive forces between the carbon group and the α-exocyclic double bond. The increase in the integral intensity of the carbonyl IR-absorption and the shift of the absorption maximum in the direction of high frequencies in γ-butyrolactone ((III), (Table 1)) is apparently explained by the anomeric effect [12, 13]. The possibility of an incidence of this effect was shown by a calculation of molecular orbitals with the optimum minimization of the geometric parameters of β-, γ-, δ-, and ε-cyclic lactones, lactams, and thiolactams [10]. From this point of view, the electronic theory of the anomeric effect includes the orbital interaction between the p-electrons of the carbonyl oxygen atom and the antibonding σ*-orbital of the adjacent —C—O bond, the p-σ* C—O overlapping being the greater the smaller the value of the angle bd and, correspondingly, the greater the difference between the angle cd and bd ((I) and (II), (Table 2)).

Correspondingly, the values of $A\nu_{C=O}$ and $\nu_{C=O}$ of the lactone carbonyl ((III), (Table 1)) will rise in comparison with the cyclic ketone (I), since with the change in the hybridization of the carbon atom of the carbonyl group the C=O bond becomes shorter, while the oxygen atom of the carbonyl group experiences a deficiency of electrons.

The above mentioned changes in the integral intensity and frequency of the absorption band of the carbonyl groups in the model compounds (I-III) (see Table 1) make it possible to explain the increase and decrease in $A\nu_{C=O}$ and $\nu_{C=O}$ in the guaianolide derivatives and their derivatives that were investigated (IV-XIII). The increase in the values of $A\nu_{C=O}$ and $\nu_{C=O}$ in the guaianolides with an α-methyl group in the γ-lactone ring (X-XII) as compared with guaianolides (IV-IX) is, in all probability, explained by the angular strain of the cyclic system which initiates an anomeric effect. This is confirmed by the substantial difference in the angles cd and bd (8°, Table 2) in guaianolides (XIV) and (XV) relative to the sesquiterpene lactone (XVI) (4.6°).

In guaianolides with an α-exomethylene bond at C-11 (IV-IX), the decrease in the IR-spectral characteristics of the lactone carbonyl that are under consideration is, in a similar manner to those of α,β-unsaturated cis-stabilized ketones [11], caused by a possible influence of the van der Waals repulsive forces between the lactone carbonyl and the exomethylene group.

Thus, on the basis of an anlaysis of the values of $A\nu_{C=O}$ and $\nu_{C=O}$ of ring C of the natural guaianolides (IV-VIII) and according to the concept of internal strain [9, 14, 15], it may be considered that a γ-lactone ring with an α-exocyclic double bond is energetically less stable than a γ-lactone ring with an α-alkyl substituent. This conclusion is confirmed by the higher capacity for taking part in addition reactions of an exocyclic double bond at C-11 as compared with one at C-4 or C-10 [16].

A further consideration of the figures of Table 1 leads to the following results. In an acyclic side chain at C-8, the integral intensity of the absorption band of an α,β-unsaturated ester carbonyl rises, and the absorption maximum shifts in the low-frequency direction (IV, XI) relative to guaianolides in which there is no terminal vinyl group at C-17 (V, XII). Thus, for example in elegin (IV) *A*  $A\,{-O-\overset{O}{\overset{\|}{C}}-C=CH_2} = 4.0$ pr.u, $\nu = 1720\ cm^{-1}$, and in hyrcanin (V) *A*  $A\ O-\underset{O}{\underset{\|}{C}}-C- = 3.40$ pr.u, $\nu = 1755\ cm^{-1}$. A similar change in the IR-spectral characteristics of an ester carbonyl at C-8 is observed from a comparison of dihydroelegin (XI) and hexahydroelegin (XII).

The observed change in the values of A and ν corresponding to the absorption of an acyclic α,β-unsaturated ester carbonyl in compounds (IV) and (XI) is apparently due to conjugation effect, which is possible when the $-C=O$ and $-C=CH_2$ substituents are coplanar.

EXPERIMENTAL

IR spectra were recorded on a UR-20 double-beam infrared spectrometer using NaCl prisms (1600-1850 cm^{-1} region). The spectral slit width in the 1600-1800 cm^{-1} interval was 8 cm^{-1}. The rate of scanning was 25 cm^{-1}/min.

To exclude intermolecular associations lowering the accuracy of the measurement of A, the spectra were recorded in dilute solutions the concentrations of which were ranged from 0.01 to 0.05 M.

Standard nondismountable cells with NaCl windows were used. The thicknesses of the absorbing layers were 0.038, 0.060, 0.055, and 0.500 cm. The solvent was carefully purified and dried with chloroform.

The integral intensities were measured by Bourgin's method [17]. The error of the intensity measurements was 5%.

SUMMARY

1. The frequencies and integral intensities of the IR bands of the stretching vibrations of the lactone acyclic ester carbonyls at C-8 of ten natural guaianolides and their derivatives, and also of three model compounds have been studied.

2. The most probable interpretation of the change in the values of $A\nu_{C=O}$ and $\nu_{C=O}$ of the lactone carbonyl has been proposed. In elegin and some of its derivatives – acroptilin, chlorohyssopifolin B, and eleganin – the lowering of the values of $A\nu_{C=O}$ and $\nu_{C=O}$ in comparison with dihydroelegin, hexahydroelegin, and the hydroxylactone of cynaropicrin is due to nonvalent interactions of the lactone carbonyl with the α-exocyclic double bond.

The increase in $A\nu_{C=O}$ and $\nu_{C=O}$ in dihydroelegin, hexahydroelegin, and the hydroxylactone of cynaropicrin is due to a deformation of the O–C=O angle of the γ-lactone ring.

3. It has been shown that in an acyclic side chain at C-8 an increase in the integral intensity and a decrease in the frequency of the absorption of and α,β-unsaturated ester carbonyl relative to guaianolides in which there is no terminal vicinal group at C-17 is due to a conjugation effect.

LITERATURE CITED

1. M. E. Perel'son, Yu. N. Sheinker, and L. A. Savina, Spectra and Structures of Coumarins, Chromones, and Xanthones [in Russian], Meditsina, Moscow (1975), p. 66.
2. L. Ananthasubramanian, H. Gopinath, and S. C. Bhattacharyya, Indian J. Chem., 25, 380 (1986).
3. F. H. Coffe, B. P. Straughan, C. J. Timmons, W. F. Forbes, and R. Shilton, J. Chem. Soc., B, 1146 (1967).
4. A. R. Katritzky, R. F. Pinzelli, and R. D. Topsom, Tetrahedron, 18, No. 13, 3449 (1972).
5. L. A. Kotorolenko, A. P. Gordenina, A. F. Rekagieva, and L. A. Kiprianova, Zh. Prikl. Spektrosk., No. 5, 366 (1966).
6. T. Burer and H. H. Gunthard, Helv. Chim. Acta, 39, 356 (1956).
7. H. K. Hall and R. Zbinden, J. Am. Chem., Soc., 80, 6428 (1958).
8. É. Eliel, Stereochemistry of Carbon Compounds, McGraw-Hill, New York (1962) [Russian translation], Mir, Moscow (1971), p. 48.
9. H. Becker, Einführung in die Elektronentheorie organisch-chemischer Reaktionen, 3rd edn., VEB Deutscher Verlag der Wissenschaften, Berlin (1974) [Russian translation], Mir, Moscow (1977), p. 310.
10. L. N. Lauritzen, H. B. Burge, P. Hofman, and H. Schmidt, Helv. Chim. Acta, 68, 76 (1985).
11. R. R. Erskine and E. S. Waight, J. Chem. Soc., 3425 (1960).
12. V. G. Dashevskii, The Conformational Analysis of Organic Molecules [in Russian], Khimiya, Moscow (1982), p. 215.
13. N. S. Zefirov, Zh. Vses. Khim. Obshchestva im. D. L. Mendeleeva, No. 3, 261 (1977).
14. H. Brown, J. H. Brewster, and H. Schecter, J. Am. Chem. Soc., 76, 467 (1950).
15. H. K. Hall and A. K. Schneider, J. Am. Chem. Soc., 80, 6409 (1958).
16. I. D. Sham'yanov, O. Mallabaev, and G. P. Sidyakin, Khim. Prir. Soedin. 442 (1978).
17. D. A. Ramsay, J. Am. Chem. Soc., 74, No. 1, 72 (1952).
18. P. Nagy, Acta Chim. Acad. Sci. Hung., 108, No. 4, 401 (1981).
19. J. P. Declercq, G. Germain, and M. V. Meerssche, Acta Crystallogr., 36, 190 (1980).
20. R. C. Pettersen and H. L. Kim, J. Chem. Soc. Perkin Trans., II, No. 12, 1399 (1976).