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CIRCULAR DICHROISM OF SOME SESQUITERPENE

LACTONES OF THE GERMAGRANE TYPE

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The CD spectra of a series of germacranelides have been considered, and the parameters of the Cotton effects observed have been correlated with the stereochemistries of the compounds studied. The applicability for germanocranolides of the Waddell-Stocklin-Geissman rule is discussed.

The empirical rules used for determining the stereochemistry of the lactone ring in sesquiterpenoids such as Samek's rule in NMR spectroscopy [1, 2] or the Waddell-Stocklin-Geissman rule in CD spectroscopy [3] do not always give correct information.

Cases of anomalous behavior have been reported among the guaiene and eudesmane lactones, but they are particularly numerous in the germacranelide series, which is due to the high conformational flexibility of the germacrane skeleton.

In order to correlate features of the spatial structures of the germacranelides with the parameters of their Cotton effects, we have considered the CD spectra of a number of lactones: tanachin (I), tamirin (II), tavalin (III), deacetyl-laurenobiolide (IV), mucrin (V), dihydromucrin (VI), mucronin (VII), and balchanolide (VIII), and a bislactone - myco-guaianolide (IX), the structures of which have been described previously [4-7].

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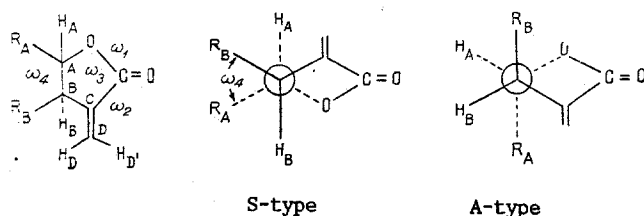
In the CD spectra of compound (I-V), each containing a conjugated lactone group, there are Cotton effects (CBs) in the 260-240 nm region due to a $n \rightarrow \pi^*$ transition in the α -methylene- γ -lactone chromophores.

For sesquiterpene lactones, Geissman et al., [3] correlated the sign of a given CD with the position and nature of the linkage of an α -methylene- γ -lactone ring in the following way:

| Ring linkage | cis | trans |
|--------------|-----|-------|
| 6-7 | + | - |
| 7-8 | - | + |

According to this rule, in the CD spectra of C_8 -trans-lactonized compounds there should be positive Cotton effects. However, results that we have obtained do not agree with this rule. In the CD spectra of compounds (I-V) negative Cotton effects are observed in the 250-260 nm region in spite of the trans-linkage of the lactone ring. These infringements of Geissman's rule can be explained in the following way. It is known that the sign of a lactone CE is determined by the chirality of the $C_D=C_C-C=O$ chromophore [8] and its torsional symbol and depends not only on the stereochemistry of the lactone ring but also on the conformation of the neighboring decadiene ring. It has been shown by x-ray structural analysis that the torsional angles ω_2 ($C_D=C_C-C=O$) and ω_3 ($C_C-C_B-C_A-O$) have the same signs and are mutually connected with the torsional angle ω_4 ($R_B-C_B-C_A-R_A$) [9-10].

Depending on the magnitude of the torsional angle ω_4 , the γ -lactone ring is capable of adopting two main conformations: the S conformation when the torsional angle $\omega_4 \leq 120^\circ$ and the A conformation when $\omega_4 \geq 120^\circ$ [1, 2]



Samek [1, 2] showed that in determining the cis-trans linkage of the lactone ring from NMR results using the values of the allyl and vicinal constants, the type of lactone conformation must also be brought into consideration.

An equally important role is played by the conformation of the ring when using the signs of the CBs in the 250 nm region to determine the nature of the linkage of the lactone ring.

Making an analogy with the conclusions drawn by Samek in an analysis of NMR results [1, 2], we have suggested that Geissman's rule is not observed in those cases where C_6 -trans-lactonized germacranolides have the A conformation ($\omega_4 \geq 120^\circ$) and C_6 -cis- and C_8 -trans-lactones the S conformation ($\omega_4 \leq 120^\circ$).

It is just the different conformations of the lactone ring that explain the opposite signs of the lactone CE at 250 nm for the germacranolides eupafornonin and eupatolide [9], in spite of the fact that both have a C_6 -trans-linked lactone ring.

C_8 -Lactonized germacranolides are conformationally even more labile than the C_6 -lactones, and if there is an ester group at C_6 then, depending on its size and position relative to the plane of the exomethylene group the lactone ring may adopt either the S or the A conformation [1].

In each of the lactones studied (I-V) there is an α -hydroxy group at C_6 stabilizing the S conformation, when the torsional angle of the $C=C-C=O$ group and, consequently, the observed Cotton effects in the 250 nm region have negative values, and Geissman's rule is not obeyed by these lactones.

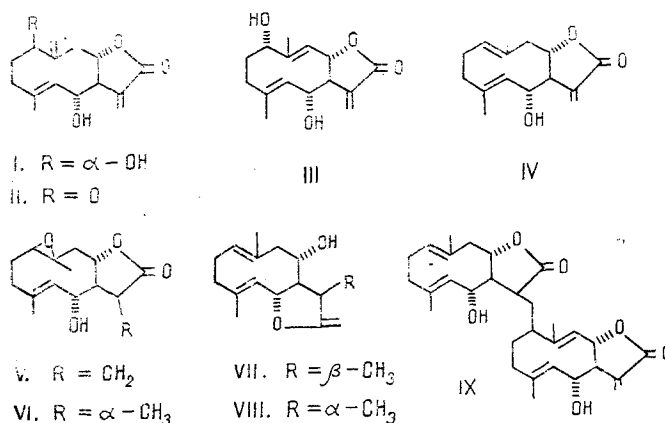
Thus, in order to obtain unambiguous information relative to the stereochemistry of the lactone rings in germacranolides combined use must be made of the methods of CD and NMR spectroscopy. Each of the germacranolides considered (apart from mucrin) has two double bonds in the central ring. In the CD spectra of the germacranolides, the diene system appears in the form of two CBs of opposite sign in the 220 and 200 nm regions [11], the latter

sometimes being located below 200 nm, when it is difficult to record it because of instrumental limitations.

The positive Cotton effects in the 220 nm region in the CD spectra of compounds (IV), (VII), and (VIII) with endocyclic double bonds indicate the trans-trans orientations of the dienic systems.

In tanachin, a (+)CE also appears in the 222 nm region and a (-)EC at 208 nm, in spite of the exocyclic nature of the double bond at C₁₀. This indicates a slight change in the conformation of the cyclodecadiene moiety when an endocyclic double bond is converted into an exocyclic one.

Tavulin (III) is identical in structure with deacetyllurinol [12]. The CD spectrum of (III) contains two negative Cotton effects, in the 236 and 208 nm regions, which is characteristic for a cyclodeca-trans-4(5),cis-9(10)-diene system. The lactone CE in the 250 nm region is not shown because it is masked by a strong broad band at 236 nm.



Mucronin (VII) and balchanolide (VIII) are isomeric in structure and differ only by the orientation of the CH₃ group at C₁₁. As can be seen from the figures given below, the change in the absolute configuration at C₁₁ has a pronounced effect only on the intensity, without causing an inversion of the sign of the CE in the CD spectra of (VII) and (VIII), since in the 220 nm region in addition to the CE due to a $n \rightarrow \pi^*$ transition of the saturated lactone chromophore there is also a CE due to the $\pi \rightarrow \pi^*$ transition of the enone system.

| Compound | λ_{\max} , nm | $\Delta\epsilon$ | Compound | λ_{\max} , nm | $\Delta\epsilon$ | |
|--------------|-----------------------------|------------------|---------------------|-----------------------|------------------|-------|
| I. Tanachin | 256 | -1,57 | VI. Dihydromucrin | 221 | -0,85 | |
| | 222 | +5,64 | | 204 | +6,31 | |
| | 207 | -2,08 | | 218 | +22,6 | |
| II. Tamirin | 323 | -0,67 | VII. Nucronin | 219 | +2,55 | |
| | 263 | -1,53 | | VIII. Balchanolide | 253 | -1,49 |
| | 211 | +29,7 | IX. Mycoguaianolide | | 220 | +11,7 |
| III. Tavulin | 256 | -1,97 | | 200 | -5,85 | |
| | IV. Deacetyllaurenobilidine | 208 | | -16,4 | | |
| | | 257 | | -0,38 | | |
| 211 | | +6,92 | | | | |
| 253 | | -1,75 | | | | |
| V. Nucrin | 213 ^{sh} | +6,11 | | | | |
| | 202 | +12,2 | | | | |

EXPERIMENTAL

CD spectra were recorded on a JASCO J-20 spectropolarimeter. The concentration of the solutions was 1 mg/ml, with cell thicknesses of 0.1, 0.05, and 0.01 cm. Methanol was used as the solvent. The lactones were isolated by literature methods [4-7].

SUMMARY

1. The trans-trans orientation of the dienic system in mucronin and balchanolide and the presence of a trans-4(5),cis-9(10) system in tavulin have been determined from CD results.

2. A change in the absolute configuration at C₁₁ in saturated C₆-trans lactones - balchanolide and mucronin - affects only the intensity of the Cotton effect at 220 nm without causing an inversion of its sign.

3. Geissman's rule is not observed in C₈-trans germacranolides with 6 α -hydroxy groups.

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TRITERPENOIDS OF THE LEAVES OF *Betula pendula* FROM DIFFERENT GROWTH SITES

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A comparative study has been made of the triterpene fraction of the unsaponifiable part of ethereal extracts of five samples of the leaves of *Betula pendula* collected in various regions of the Soviet Union. Together with known sterols and triterpenoids, two new compounds have been isolated - 12 β ,20(S),25-trihydroxydammar-23-en-3-one and dammar-25-ene-3 α ,12 β ,17 α ,20(S),24 ξ -pentaol, the structures of which have been determined on the basis of spectral characteristics and chemical transformations.

The leaves of *Betula pendula* Roth. were first studied for their triterpenoid content by the German chemists Fischer and Seiler. They detected two previously unknown triterpene alcohols of the dammarane series - betulafolienetriol (dammar-24-ene-3 α ,12 β ,20(S)-triol) (I) and betulafolienetetraol (dammar-24-ene-3 α ,12 β ,17 α ,20(S)-tetraol) (II), the total amount of which was 0.8% of the weight of the crude birch leaves. The main component was the betulafolienetriol, the amount of which was seven times that of the betulafolienetetraol [1]. Triterpene alcohols of this type are particularly interesting because of their structural similarity to the aglycons of the panaxosides - the glycosides of ginseng. It must be mentioned that betulafolienetriol differs from the protopanaxadiol [2] only by the orientation of the hydroxy group at C-3. From these two alcohols (I) and (II) synthetic analogs of the panaxosides have been obtained which have exhibited physiological activity equal to the activity of the native panaxosides [3].

B. pendula grows over the major part of the territory of the USSR. However, the leaves of *B. pendula* collected in the boundary area of this birch, in Eastern Siberia that we inves-

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