CIRCULAR DICHROISM OF SOME CHLORINE-CONTAINING GUAIANOLIDES

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A study of the circular dichroism of chlorine-containing guainolides has shown that a negative Cotton effect in the 260-nm region correlates with the trans-linkage of the lactone ring in acroptilin, hyrcanin, chlorohyssopifolin B, elegin, and biebsanin. It has been established that this nature of the linkage does not change on relactonization and hydrogenation. A chloromethylene substituent at C_4 causes a bathochromic shift of the lactone Cotton effect.

The present paper considers the interrelationship between the nature of the circular dichroism (CD) curves and the stereochemical features of chlorine-containing sesquiterpenoids of the guaiane type: acroptilin (I), hyrcanin (centaurepensin, chlorohyssopifolin A) (II), chlorohyssopifolin B (III), elegin (linichlorin A) (IV), biebsanin (V) and their derivatives [1-6]. For comparison we also recorded the CD spectrum of chrysartemin B (VI) — a guaianolide containing no chlorine [7]. The CD curves for some of the lactones that we have considered are shown in Fig. 1.

The CD spectra of the lactones show a Cotton effect (CE) in the 250-270-nm region which is due to a n → π* transition in the α-methylene-γ-lactone chromophore, the sign of which depends on the nature of the B/C ring linkage [8]. The results given below show that lactones (I-VI) have a negative CE in the 250-270-nm region which is characteristic for the trans-linkage of the lactone ring. It has been reported previously that in the pseudoguaianolides ambrosiol and apoludin (cis-linkage of rings B/C), the 4α-hydroxy group causes an anomalous change in the sign of the lactone Cotton effect [8]. In the lactones that we have studied (II-IV, and V) a hydroxy group at C_4 has no effect on the sign of the lactone CE, while the presence of a chloromethylene substituent at C_4 causes a bathochromic shift of the latter in the CD spectra of (II-IV) as compared with the lactones (I), (V), and (VI) containing no such substituent (Table 1 and Fig. 1).

In the 230-220-nm region a (—) CE due to a π → π* transition in the exocyclic double bond at C_{10} appears in the CD curves of compounds (I-III). In elegin, this CE is masked by a positive CE connected with the unsaturated ester group at C_8.

From the products of the hydrolysis of elegin (4% aqueous KOH at room temperature for 24 h) we obtained the hydroxy lactone (IX), $C_{15}H_{19}O_5Cl$, with mp 183-184°C, which was characterized as a relactonization product. With this nature of the closure of the lactone ring (C_7—C_8) a positive CE at 255 nm shows the trans linkage of rings B/C in (IX).

After the treatment of (IV) with sodium tetrahydroborate, the exomethylene bond of the lactone ring was reduced, and in the CD spectrum of dihydroelegin (X) the lactone CE had shifted to 232 nm and the sign had become positive, which, according to the sector rule, again confirms the trans-linkage of the lactone ring in (X).

In the 200-nm region there is an intense CE due to several electron transitions: n → π* of the saturated ester group and π → π* and σ → π* of an unsaturated lactone grouping and a double bond. The saponification of (IX) caused a decrease in the intensity of the CE at 200 nm and the hydrogenation of (X) caused a change in the sign of the latter, in addition.

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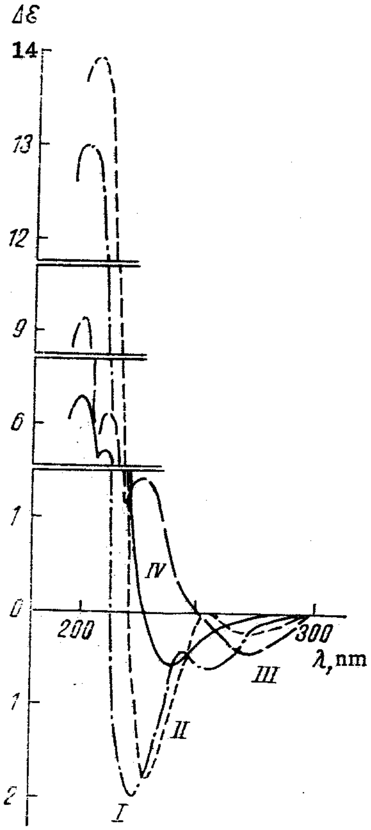
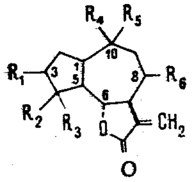


Fig. 1. CD curves of acroptilin (I), chlorohyssopifolin B (II), elegin (III), and biebsanin (IV).

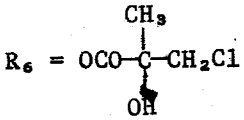
TABLE 1

Compound	λ_{max}, nm	Δε	Compound	λ_{max}, nm	Δε
Acroptilin (I)	256 223 200	−0,54 −2,12 +13,4	Chrysartemin B (VI)	248 208 200	−1,03 +2,18 +4,26
Hyrcanin (II)	263 225 201	−0,56 −1,90 +14,5	Elegin acetate (VII)	264 233 216 206	−0,37 −0,17 +5,30 +6,68
Chlorohyssopifolin B (III)	269 230 205	−0,17 −1,81 +12,7	Elegin diacetate (VIII)	260 232 215 205	−0,36 −0,28 +2,07 +5,34
Elegin (IV)	264 216 205	−0,44 +6,41 +9,40	Hydroxylactone from elegin (IX)	255 223 203	+0,27 −4,55 ∓5,48
Biebsanin (V)	249 208 200	−0,68 +5,32 +6,60	Dihydroelegin (X)	233 215 205	+0,22 −1,21 −4,20



I. $R_1 = OH$;
$R_2R_3 = -O-CH_2-$;
$R_4R_5 = {=}CH_2$

II. $R_1 = OH$; $R_2 = CH_2Cl$;
$R_3 = OH$; $R_4R_5 = {=}CH_2$

(I, II) $R_6 =$

$R_6 = OCO-\overset{CH_3}{\underset{OH}{C}}-CH_2Cl$

III. $R_1 = OH$; $R_2 = CH_2Cl$; $R_3 = OH$
$R_4R_5 = {=}CH_2$; $R_6 = OH$

IV. $R_1 = OH$; $R_2 = CH_2Cl$; $R_3 = OH$

$R_4R_5 = {=}CH_2$; $R_6 = OCO-\overset{CH_3}{C}{=}CH$

V. $R_1 = Cl$; $R_2 = CH_3$; $R_3 = OH$
$R_4 = CH_3$; $R_5 = OH$; $R_6 = OH$
epoxy group at C_1-C_2

VI. $R_2 = CH_3$; $R_3 = OH$; $R_5 = OH$; $R_6 = H$
epoxy groups at C_1-C_{10} and C_2-C_3

EXPERIMENTAL

The CD spectra were recorded on a JASCO J-20 polarimeter. The concentration of the solution was 1 mg/ml and the cell thicknesses 0.5, 0.05, and 0.01 cm. Ethanol was used as solvent.

SUMMARY

It has been established from CD spectra that a negative Cotton effect in the 250-270-nm region correlates with the trans-linkage of the lactone ring in guaianolides (I-VI), and that the trans-linkage of the rings B/C is retained on relactonization and hydrogenation.

A chloromethylene group at C_4 shifts the lactone Cotton effect bathochromically in the CD spectra of lactones (II-IV).

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