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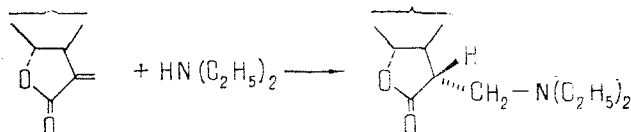
CIRCULAR DICHROISM OF THE PRODUCTS OF THE AMINATION OF LACTONES

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The circular dichroism method has been used to study the products of the amination of sesquiterpene lactones containing α -methylene- γ -lactone groupings. Analysis of the results obtained has shown that in all the lactones considered the amination reaction takes place with the predominant formation of one of the possible stereochemical forms of the product of the addition of the amine to the exomethylene group of the lactone ring, namely, that having the 11S configuration.

Sesquiterpene lactones with a γ -lactone ring conjugated with an exomethylene group readily add secondary amines by the Michael reaction [1]:



This reaction takes place with the hydrogen atom adding to the more substituted carbon atom and the N-ethyl residue to the less substituted one, forming a new asymmetric center at C₁₁, the configuration of which is unknown. This reaction is frequently used to obtain soluble forms of this group of lactones and in the separation of mixtures of lactones.

In stereochemical investigations the stereospecific reactions of reduction by sodium tetrahydroborate and diazomethane of an exomethylene bond conjugated with a γ -lactone grouping are used with success [2, 3]. It appeared of interest to establish whether the amination reaction is stereospecific and to determine the configuration of the newly formed asymmetric center at C₁₁. With this aim, we have considered the circular dichroism (CD) spectra of guaianolides containing the α -methylene- γ -lactone grouping and the products of their amination at room temperature. The CD spectra of the following guaianolides were recorded: rupicolin A (1), rupicolin B (2), ajanin (3), ajadin (4), arteglaasin (5), cumambrin (6), chrysartemin (7), the eudesmanolide artecalin (8), tetrahydrorupicolin B (9), dihydroajanin (10), and dihydrochrysartemin (11). In the spectra of these lactones in the 250-270 nm region a Cotton effect (CE) is observed which is due to an $n \rightarrow \pi^*$ transition in the α -methylene- γ -lactone chromophore the sign of which depends on the nature of the linkage of rings B/C [4]. All the compounds studied had the trans linkage of the lactone rings closed at C₆. This

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TABLE 1

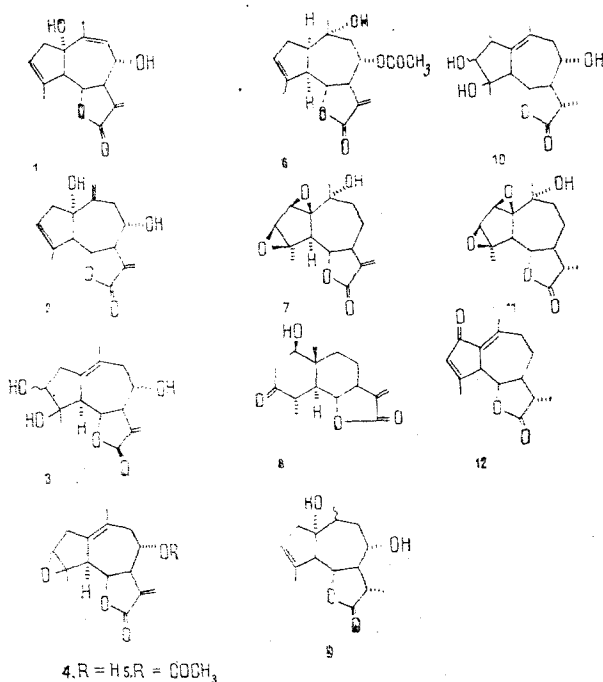
Compound	Methanol		Methanol + (C ₂ H ₅) ₃ NH	
	λ_{max} , mm	$\Delta\epsilon$	λ_{max} , mm	$\Delta\epsilon$
1. Rupicolin A	260	-0.40	260	-
	225	-0.60	224	+0.48
	198	+24.7	198	-50.9
2. Rupicolin B	266	-0.19	265	-
	225	-1.35	228	+0.16
	198	+21.8	198	+33.6
3. Ajanin	265	+0.29	265	-
	233	-2.30	230	+0.18
	215	+1.87	-	-
4. Ajadin	200	-5.87	204	-12.6
	265	+0.21	265	-
	233	-1.80	231	+0.22
5. Arteglasin	206	+12.8	206	-2.20
	264	+0.16	264	-
	229	-1.23	230	+0.17
6. Cumambrin	208	+9.04	208	-2.41
	257	-1.12	257	-
	213	+2.00	226	+0.28
7. Chrysartemin	204	+10.0	209	-1.08
	255	-1.16	255	-
	235	-1.18	235	-0.22
8. Artecalin	209	-4.65	218	+0.88
	203	+5.17	212	+2.15
	287	+0.80	286	+0.64
9. Tetrahydorupicolin B	250	-0.76	250	-
	204	+9.25	218	+1.66
	224	+0.44	211	+1.89
10. Dihydroajanin	205	-5.96	224	+0.44
	228	+0.63	205	-1.08
	205	-12.6	228	+0.63
11. Dihydrochrysartemin	218	+0.94	207	-12.6
	325	-0.07	218	+0.97
	246	+1.58	257	-0.24
12. Leucomisin	229	+0.78	357	+0.60
	208	-2.19	230	+5.33
			210	+0.89

type of linkage is characterized by a negative CE in the 250-270 nm region, as was in fact observed in the CD spectra of the compounds considered (Table 1). Exceptions were ajanin, ajadin, and arteglasin (the trans linkage of rings B/C in them has been shown by chemical transformation), in the CD spectra of which there are positive CEs at 265 nm. This deviation from the general rule is possibly due to the presence of a $\Delta^{1,10}$ double bond in ring B, which makes the conformation of the seven-membered ring more fixed. When an amine in methanolic solution was added to one of the compounds under investigation, it added to the exomethylene bond of the lactone, ring and in the CD spectrum it was possible to observe a gradual decrease of the CE in the 250-270 nm region and the appearance of an additional CE in the 220-230 nm region due to the $n \rightarrow \pi^*$ transition of the saturated lactone chromophore.

Since the amination reaction takes place under mild conditions without heating, the lactone ring is not broken and the trans linkage of rings B/C is retained. Under these conditions, according to the sector rule [5] and by analogy with the eudesmanolides [6] a positive CE in the 220-230 nm region may be connected with the α orientation of the $-\text{CH}_2-\text{N}(\text{C}_2\text{H}_5)_2$ group at C₁₁. This permits the assumption that the amination reaction takes place with the predominant formation of one of the possible stereochemical forms of the product of the addition of the amine to the lactone, namely that with the 11S configuration. (See following page.)

To confirm the stereospecificity of the amination reaction, we compared the CD spectra of some of the lactones studied (II, IV, and VII) after reduction with sodium tetrahydroborate and with diethylamine. It is known that in compounds reduced by sodium tetrahydroborate (IX-XI), the newly formed asymmetric center at C₁₁ has the 11S configuration (α -orientation of the CH₃ group), which is characterized by a positive CE in the 220 nm region provided that rings B/C have the trans linkage.

It can be seen from the results presented in Table 1 that after treatment of the lactone with both sodium tetrahydroborate and with the amine, a positive CE appeared in the CD spec-



tra in the 220-230 nm region, i.e., the asymmetric center formed at C₁₁, has the same configuration in the two cases.

It must be mentioned that an amine readily reacts also with diene groupings if they are present in lactones, and this must be taken into account in the interpretation of the results obtained. To illustrate this fact, Table 1 gives the spectrum of leucomisin and of its amination product.

EXPERIMENTAL

The CD spectra were recorded on a JASCO J-20 spectropolarimeter. Solutions in methanol at a concentration of 1 mg/ml were used, with cell thicknesses of 0.1, 0.02, and 0.01 cm. In the amination reaction, two drops of freshly distilled diethylamine were added to 3 ml of a methanolic solution of the lactone. The CD measurements were made an hour, a day, and two days after the addition of the amine. In the spectra of compounds (I-VI), the disappearance of the Cotton effect in the 260-270 nm region caused by the amination of the exomethylene bond of the lactone ring and the appearance of the positive CE in the 230-220 nm region took place during an hour, while the analogous changes in the CD spectra of compounds (VII and VIII) could be observed after a day.

SUMMARY

It has been shown that the addition of diethylamine to the exocyclic double bonds of α,β -unsaturated lactones takes place with the predominant formation of the 11S isomers.

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