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CIRCULAR DICHROISM OF GUAIANOLIDES AND THE PRODUCTS OF THEIR AMINATION

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The presence of an α-oriented hydroxy group at C_8 in a guaianolide promotes the stereospecificity of the amination of an exomethylene bond linked with the γ-lactone grouping. The addition of morphiline and of piperidine to the exomethylene bond of the lactone ring of a guaianolide containing an α-oriented hydroxy group at C_8 takes place with the preferential formation of the 11S isomer.

Continuing a study of the stereospecificity of amination of an exomethylene bond conjugated with a γ-lactone grouping [1], we have investigated the addition of the cyclic secondary amines morphiline and piperidine to unsaturated lactones of the guaiane type: rupicolin A (I), rupicolin B (II) ajanin (III), ajadin (IV), and chrysartemin (V), and a eudesmanolide — artecalin (VI).

With this aim, the circular dichroism (CD) spectra of the lactones (I-VI) and their amination products have been recorded. The results obtained have enabled us to refine the conclusion drawn previously relative to the stereospecificity of the amination of unsaturated lactones [1].

As can be seen from Table 1, in the CD spectra of the lactones considered a negative Cotton effect (CE) is observed in the 250-270 nm region which is due to the $n\rightarrow\pi^*$ transition in the α-methylene-γ-lactone chromophore, confirming the trans-linkage of rings B/C.

In ajanin and ajadin, the double bond in ring B causes an inversion of the CE in the 265 nm region. The presence of oxygen-containing substituents at C_4 may also change the sign of the lactone CE, as has been reported previously for the pseudoguanolides ambrosiol and anoludin [2].

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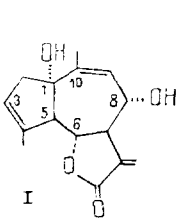
TABLE 1. Results of the Measurement of the Circular Dichroism of Lactones and Their Amination Products

Compound	Methanol		Methanol + piperidine		Methanol + morpholine	
	λ_{max}, nm	$\Delta\varepsilon$	λ_{max}, nm	$\Delta\varepsilon$	λ_{max}, nm	$\Delta\varepsilon$
1. Rupicolin A	260	—0,36	260	—	260	—
	223	—0,68	225	+0,37	225	+0,32
2. Rupicolin B	266	—0,15	266	—	266	—
	226	—1,65	235	+0,10	230	+0,12
			216	—0,89	216	—1,06
3. Ajanin	265	+0,24	265	—	265	—
	233	—2,12	230	+0,21	229	+0,20
	216	+1,96	210	—2,73	209	—3,47
4. Ajadin	265	+0,23	265	—	265	—
	232	—1,73	229	+0,24	230	+0,20
	207	+12,3	212	—2,29	209	—2,57
5. Chrysartemin B	250	—1,02	250	—	250	—
	205	+4,90	211	+1,83	210	+0,68
6. Artecalin	287	+0,88	285	+0,81	286	+0,86
	250	—0,84	250		250	—
	204	+7,95	206	+1,70	216	+1,85

The amination by morphiline and piperidine of an exomethylene bond conjugated with a γ-lactone grouping took place under the same mild conditions as with diethylamine [1]. When piperidine and morphiline were added to the lactones (I-IV), the CE in the CD spectra of these compounds in the 260 nm region decreased to zero, and a positive CE due to the n—π* transition of a saturated lactone chromophore appeared in the 230 nm region. A positive CE in the 230 nm region, under the conditions of the trans-linkage of the lactone ring, indicates the S configuration of the asymmetric center at C_{11} formed on amination.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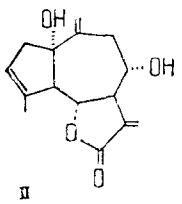
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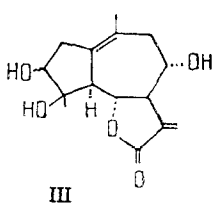
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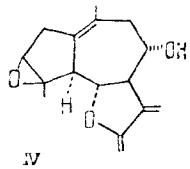
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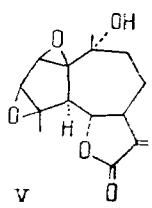
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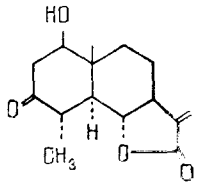
VI

The lactones (I-IV) contain an α-oriented hydroxy group at C_8 which, as can be seen from models, closely approaches the exomethylene bond of the lactone ring. The screening of the exomethylene bond by an α-oriented hydroxy group at C_8 is also shown by the NMR spectra [3]. As a result of this, the approach of the amine molecule to the exomethylene bond from the side of the hydroxyl is hindered. This situation promotes the stereospecificity of the addition reaction, which takes place with the formation predominantly of one of the two possible stereochemical forms of the product of the addition of the amine to the lactone – namely, that with the 11S configuration.

In the CD spectra of chrysartemin B (V) and artecalin (VI) no CE appeared in the 230 nm region after the addition of an amine, in spite of the fact that addition to the exomethylene bond did take place, since the CE in the 250 nm region fell to zero. Such a behavior of chrysartemin B and artecalin is probably due to the fact that there is no hydroxy group of C_8 and the amine molecule can approach from both sides of the exomethylene bond. As a result, approximately equal amounts of addition products of the 11S and 11R configurations are formed.

The amines that we studied differ in basicity, which is reflected in the rates of amination. Thus, for example, with morpholine the reaction took place far more slowly than with diethylamine and piperidine.

SUMMARY

Circular dichroism spectra were recorded on a JASCO J-20 spectropolarimeter. The concentration of the solutions was 1 mg/ml and the thicknesses of the cells 0.1, 0.02, and 0.01

cm. Methanol was used as solvent. For amination, two drops of freshly distilled piperidine or morpholine was added to 3 ml of a methanolic solution of the lactone.

SUMMARY

1. It has been established that the presence of an α-oriented hydroxy group at C_8 in guaianolides promotes the stereospecificity of the amination of an exomethylene bond conjugated with a γ-lactone grouping.

2. It has been shown that the addition of morphiline and piperidine to the exomethylene bond of the lactone ring of a guaianolide containing an α-orientated hydroxy group at C_8 takes place with the preferential formation of the 11S isomer.

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CYCLIZATION AND REARRANGEMENT OF DITERPENOIDS. III. SYNTHESIS OF ISOAGATHOLACTONE AND METHYL SPONGIA-13(16),14-DIEN-19-OATE

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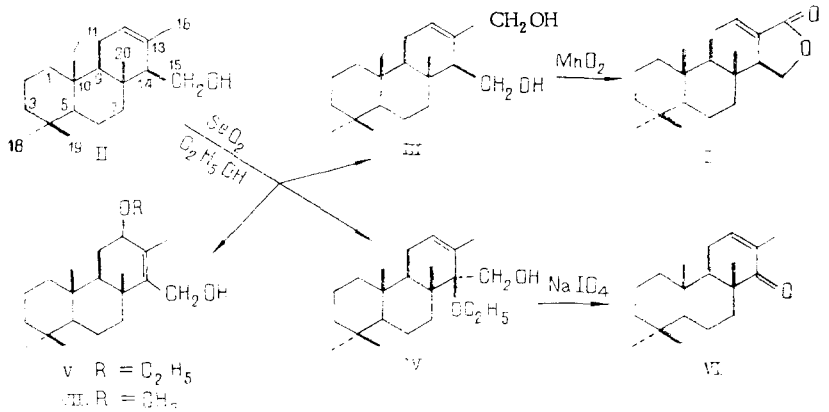
The synthesis of isoagatholactone has been effected by the successive oxidation of (14R)-isoagath-12-en-15-ol with selenium dioxide and manganese dioxide. Methyl spongia-13(16),14-dien-19-oate has been obtained by the cyclization of methyl lambertianate with 100% sulfuric or fluorosulfonic acid.

Isoagatholactone (I) [1] is the first representative of a group of tricyclic isoagathane diterpenoids detected in a natural source. At the present time, monotypical syntheses of this compound [2], of its racemic form [3], and of its antipode [4] have been performed. However, they have involved several stages and have given low yields of the lactones.

The synthesis of isoagatholactone (I) from (14R)-isoagath-12-en-15-ol (II) — its probably biogenic precursor — including as the main stage the oxidation of the C_{16}-methyl group of the alcohol (II), would be shorter and more effective. As is well known [5], the alcohol (II) is one of the products of the cyclization of a whole series of labdane diterpenoids.



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