

**STRUCTURE OF LASEROLIDE AND ISOLASEROLIDE:
REVISION OF CONSTITUTION AND DETERMINATION
OF RELATIVE AND ABSOLUTE CONFIGURATION***

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The position of the ester groups in sesquiterpene lactones laserolide (*I*) and isolaserolide (*II*) has been revised and its relative and absolute configuration determined by chemical and physical methods (NMR and CD spectroscopy). The structure *I* was confirmed by X-ray diffraction analysis. Laserolide (*I*) is the first germacranolide found in the *Umbelliferae* family, isolaserolide (*II*) is the first representative of new stereostructural group of elemanolides — 5βH,6αH,7αH,10αCH₃-elema-1,3-dien-6,12-olides.

The sesquiterpene lactones laserolide and isolaserolide were isolated by us from the underground part of the *Laser trilobum* (L.) BORKH. species¹ and, later on, assigned^{2,3} the constitution represented by the formulae *Ia* and *Ia*, respectively. Now, we have studied the stereostructure of both lactones using newly measured 200 MHz ¹H NMR and ¹³C NMR spectra of the natural lactones and some of their derivatives (for a preliminary communication see ref.⁴).

The ¹H NMR spectrum of laserolide (*I*) (Table I) afforded parameters of all protons except the methylene protons in positions 2 and 3 which formed a strongly interacting system, partly overlapped in the region δ 1.9–2.4. Also the ¹³C NMR spectrum (Table II) was fully consistent with the structure *I* or *Ia*; however, no unequivocal information on the position of the two ester groups was obtained from these data. This was determined from the *J*_{C,H} interactions in the nondecoupled ¹³C NMR spectrum of laserolide. The signal of an acetate carbonyl carbon is always split into a quartet by interactions (²*J*_{C,H} = 7 Hz) with the three methyl protons of the acetate group. For a secondary acetate there is a further interaction (³*J*_{C,H}) of the carbonyl carbon with the methine hydrogen in the >CH—O—CO—CH₃ grouping whereas no such interaction exists for tertiary acetates (fragment $\begin{array}{c} | \\ \text{—C—O—CO—} \\ | \end{array}$

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—CH₃). We checked ¹³C NMR spectra of a series of sesquiterpenic lactones and have proved that this behaviour can be used for a proof of an acetate carbonyl in the spectra (another criterion can be the chemical shift at about δ 170), particularly for distinction of primary, secondary and tertiary acetates. In primary acetates, the carbonyl carbon atom shows two further interactions ³J_{C,H} in addition to the basic splitting into the quartet. The classification of acetate groups on the basis of J_{C,H} is given in Table III. In the case of laserolide, the acetate carbonyl carbon affords a doublet of quartet at δ 169.97, split by three 7.0 Hz interactions with methyl protons and by one further interaction (3.5 Hz). Consequently, the acetate must be secondary and must be attached in position 8 whereas the angelate is bonded in position 11. These facts prove unequivocally the position of the ester groups in laserolide, correcting thus the originally suggested structure *Ia* in favour of *I*.

Pyrolysis of laserolide *I* afforded a compound identical with the isolated natural lactone isolaserolide^{1,3} (*II*). The formation of isolaserolide can be explained by Cope rearrangement, well known in the germacradienolide chemistry. Its ¹H and ¹³C NMR spectra (Table I and II) are fully consistent with the structure *II*. As follows from the mentioned chemical correlation, the position of the ester groups must be the same as in laserolide. This has been confirmed independently again by the nondecoupled ¹³C NMR spectrum: The acetate carbonyl carbon signal at δ 169.83 is again a doublet of quartet with ²J_{C,H} = 7 and ³J_{C,H} = 3.5 Hz. The observed vicinal coupling constants of protons in isolaserolide (*II*) agree best with a twist-boat conformation of the six-membered ring with relative configurations at C₍₅₎ to C₍₈₎, as shown in the formula *II*.

Laserolide (*I*) was converted into a series of derivatives. Alkaline hydrolysis afforded the known² diol *III* which on acetylation furnished the diacetate *IV* and monoacetate *V* (ref.²). As shown by ¹H NMR spectra of *IV* and *V*, the hydrolysis is accompanied by cleavage of the lactone ring followed by recyclization into the position 8. The markedly broader signals indicate the presence of more conformers and conformational interconversion of the rather flexible ten-membered ring. Such behaviour is typical for germacradienolides with lactone ring in position 8: e.g. the ¹³C NMR signals of laurenobiolide (*VI*) was markedly broadened at room temperature and at -15°C even separated signals due to four conformers appeared^{5,6}.

Oxidation of the diol *III* gave the ketone *VII*. Evidently, oxidation of the hydroxyl in position 6 was accompanied by rearrangement of the C₍₄₎=C₍₅₎ to the C₍₄₎=C₍₁₅₎ double bond as proved by the signals of C₍₁₅₎ exomethylene protons at δ 5.08 and 5.02 and an isolated AB-system of C₍₅₎H₂ protons, appearing as doublets at δ 3.28 and 3.05 (J_{5,5'} = 14.4 Hz), broadened by small allylic couplings with the exomethylene protons.

The relative configuration at C₍₆₎, C₍₇₎ and C₍₈₎ in laserolide (*I*) and isolaserolide (*II*) was determined using the cyclized derivatives *VIII*–*XI* in which the six-membered ring facilitates the conformational and configurational analysis. The diesters *VIII* and *X* were prepared by cyclization of laserolide (*I*) and there is no reason for a change

TABLE I

¹H NMR Chemical shifts and coupling constants of laserolide (I), isolaserolide (II) and some derivatives in deuteriochloroform

Proton	I	II	IV	V	VII
H-1	5.11 m	5.94 dd (17.5; 10.8)	5.02 bdd (9.5; 4.0; 1.2(3×))	5.02 m	5.35 bdd (9.0; 5.0; ≠0)
H-2		5.10 dd (17.5; 0.7)	a	a	
H-2'		5.04 dd	a	a	
H-3	1.90—2.40	(10.8; 0.7)	a	a	2.03—2.35
H-3'		5.05 m (1.4(3×); 1)	a	a	
		4.76 m (0.7(3×); 1)	a	a	
H-5	4.74 bd (10.3; 1.5(3×))	2.16 d (12.3)	4.90 bd (6.4; 1.3(3×))	4.94 um	3.29 bd ^b (14.4; ≠0)
H-6	5.38 dd (10.3; 9.4)	5.08 dd (12.3; 9.9)	5.64 bd (6.4; 2.1; 0.9)	6.76 bd (6.9; ≠0)	—
H-7	3.72 dd (11.3; 9.4)	3.37 dd (9.9; 7.7)	2.92 um	3.03 um	3.01 d (9.8)
H-8	5.28 dt (11.3; 10.8; 4.0)	5.26 ddd (9.6; 7.7; 3.8)	4.72 um	4.75 um	4.83 ddd (11.6; 9.9; 4.4)
H-9	2.86 bd (14.0; ≠0)	2.00 dd (13.9; 3.8)	a	a	2.73 dd (11.6; 4.4)
H-9'	1.84 dd (14.0; 10.8)	1.49 dd (13.9; 9.6)	a	a	1.99 t (11.6)
H-13	1.52 s	1.60 s	1.78 s	1.56 s	1.49 s
H-14	1.40 bd (1.3; ≠0)	1.04 s	1.72 bd (1.2; ≠0)	1.71 b	1.47 t (1.0)
H-15	1.74 d (1.5)	1.82 dd (1.4; 0.7)	1.57 t (1.3; 0.9)	1.59 b	5.08 m; 5.02 dt (1.5; 1.4; 0.6)
OAc:	2.07 s	2.05 s	2.10 s 2.00 s	2.01 s	—
OA _{ng} :	6.20 qq (7.3; 1.5)	6.20 qq (7.3; 1.5)	—	—	—
	1.93 p (1.5)	1.90 p (1.5)	—	—	—
	2.04 dq (7.3; 1.5)	2.01 dq (7.3; 1.5)	—	—	—

^a Parameters could not be determined; ^b H-5': 3.05 bd (14.4; ≠0).

TABLE I
(Continued)

VIII	IX	X	XI
<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
5.46 μ m	5.44 μ m	2.39 μ m (13.6; 3.4(2 \times); 1.7)	2.39 μ m (13.6; 3.4(2 \times); 1.7)
—	—	<i>a</i>	<i>a</i>
<i>a</i>	2.09 bd (10.9)	<i>a</i>	1.94 bd (11.2)
4.88 dd (11.6; 9.2)	4.79 dd (10.9; 7.9)	5.10 dd (11.6; 9.6)	5.00 dd (11.2, 9.0)
3.45 dd (9.2; 3.8)	2.83 dd (7.9; 6.3)	3.47 dd (9.6; 3.2)	2.91 dd (9.0; 3.0)
5.24 q (4.7; 4.7; 3.8)	4.16 q (6.5; 6.3; 4.8)	5.26 dt (4.5(2 \times); 3.2)	4.32 μ m
<i>a</i>	1.78 dd (14.4; 6.5)	<i>a</i>	<i>a</i>
<i>a</i>	1.61 dd (14.4; 4.8)	<i>a</i>	<i>a</i>
1.60 s	1.53 s	1.61 s	1.51 s
0.97 s	1.05 s	0.91 s	1.00 s
1.87 b	1.82 b	5.03 μ m	5.01 μ m
2.03 s	—	4.90 μ m	4.84 μ m
6.19 qq (7.2; 1.5)	—	2.04 s	—
1.92 p (1.5)	—	6.19 qq (7.3; 1.5)	—
2.00 dq (7.2; 1.5)	—	1.92 p (1.5)	—
		2.01 dq (7.3; 1.5)	—

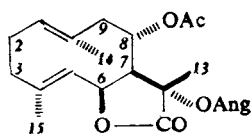
TABLE II
Carbon-13 chemical shifts of laserolide (I) and isolaserolide (II) in deuteriochloroform

Carbon	I	II
C-1	128.48 d	145.63 d
C-2	26.64 t	116.33 t
C-3	39.40 t	111.41 t
C-4	142.99 s	140.14 s
C-5	122.08 d	52.98 d
C-6	73.52 d	75.65 d
C-7	46.75 d	46.24 d
C-8	73.49 d	67.26 d
C-9	41.91 t	40.11 t
C-10	133.57 s	38.88 s
C-11	79.38 s	77.77 s
C-12	174.28 s	174.18 s
C-13	19.72 q	20.86 q
C-14	17.45 q	22.50 q
C-15	20.88 q	22.89 q
OAc	169.97 s 21.23 q	169.83 s 21.05 q
OAng	166.37 s 126.65 s 140.67 d 15.87 q 20.23 q	166.70 s 126.69 s 140.55 d 15.86 q 20.21 q

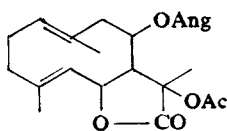
TABLE III
Classification of acetates from the splitting of their carbonyl carbons in ^{13}C NMR nondecoupled spectra

Acetate (fragment)	$\delta_{\text{C=O}}$	Multiplicity	$^2J_{\text{C,H}}$; $^3J_{\text{C,H}}$
Primary ($-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_3$)	~ 170	tq (ddq)	$7(3\times)$; $\sim 3.5(2\times)$
Secondary ($-\overset{ }{\text{C}}\text{H}-\text{O}-\text{CO}-\text{CH}_3$)	~ 170	dq	$7(3\times)$; $\sim 3.5(1\times)$
Tertiary ($-\overset{ }{\underset{ }{\text{C}}}-\text{O}-\text{CO}-\text{CH}_3$)	~ 170	q	$7(3\times)$ —

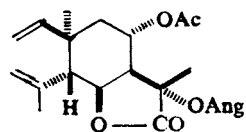
of configuration in the mentioned positions (6–8). The values of the vicinal coupling constants ${}^3J_{H,H}$ in positions 5–9 in the diester VIII indicate a flattened chair form with axial hydrogens $H_{(5)}$ and $H_{(6)}$ ($J_{5,6} = 11.6$ Hz) and equatorial hydrogens $H_{(7)}$ and $H_{(8)}$ ($J_{7,8} = 3.8$ Hz, $J_{8,9} = J_{8,9'}$ 4.7 Hz). The higher value of $J_{6,7}$ (9.2 Hz) is obviously due to flattening of the chair from by *cis*-fusion of the lactone ring.



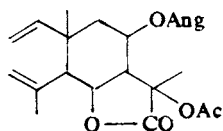
I



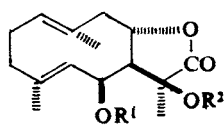
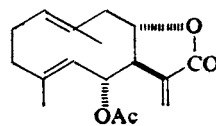
Ia



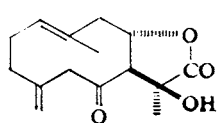
II



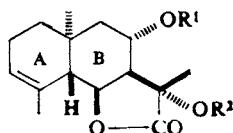
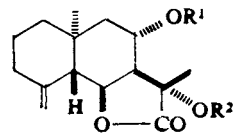
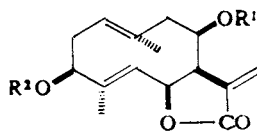
IIa

III: $R^1, R^2 = H$ IV: $R^1, R^2 = Ac$ V: $R^1 = Ac, R^2 = H$ 

VI



VII

VIII: $R^1 = Ac, R^2 = Ang$ IX: $R^1, R^2 = H$ XII: $R^1 = Bzl(NO_2)_2, R^2 = H$ X: $R^1 = Ac, R^2 = Ang$ XI: $R^1, R^2 = H$ XIII: $R^1 = Epang, R^2 = Ac$ XIV: $R^1 = COC(CH_3)(OH)CH(OAc)CH_3, R^2 = Ac$ XV: $R^1 = Epang, R^2 = H$

Ac = $COCH_3$, Ang = $COC(CH_3) = CHCH_3(Z)$,

$Bzl(NO_2)_2 = COC_6H_4(NO_2)_2(3,5)$, Epang = $COC(CH_3) - CHCH_3$

The relative configuration in positions 6, 7 and 8 thus corresponds to the formula *VIII*. Analogous conclusions hold also for the diester *X*.

Unlike laserolide (*I*), the diesters *VIII* and *X* do not relactonize at $C_{(8)}$ on hydrolysis, and the resulting diols *IX* and *XI* retain the lactone ring at $C_{(6)}$. The $^1\text{H NMR}$ spectra (Table I) exhibit characteristic changes in chemical shifts, resulting from replacement of the ester by hydroxy groups and indicate smaller conformational changes of the six-membered ring B as compared with the diesters *VIII* and *X*.

The structure *I* for laserolide has been confirmed by the X-ray diffraction analysis⁶. In crystal, laserolide molecule exists in a chair-boat conformation of the cyclodeca-(*E*)1(10), (*E*)4-diene ring with *syn*- α -oriented methyl groups at $C_{(4)}$ and $C_{(10)}$ and *cis*-6,7-fused γ -lactone ring which in envelope-shaped with $C_{(7)}$ forming the flap. The angelate group is attached to $C_{(11)}$ and the acetate to $C_{(8)}$ with 11α and 8α -configuration, respectively (for a perspective drawing see Fig. 1). A detailed comparison of the spatial arrangement of the laserolide molecule in crystal with that in solution is difficult because the $^3J_{\text{H,H}}$ values of interactions between the protons in positions 1–3 are not accessible. Nevertheless, the available values of $^3J_{\text{H,H}}$ for the positions 5 to 9 indicate similar conformations in crystal and in solution.

The absolute configuration of laserolide (*I*) was determined using two widely employed rules: 1) the benzoate rule^{7–10} and 2) the sector rule^{11,12}. According to the benzoate rule^{7–10}, the difference between the specific molar rotations of the dihydroxylactone *IX* ($[\text{M}]_{\text{D}} -17.3$) and its 3,5-dinitrobenzoate *XII* ($[\text{M}] +52.5$) indicates the *S*-configuration at $C_{(8)}$. Application of the sector rule^{11,12} to the Cotton effects observed in the region 220–225 nm in the CD spectra of *VIII* (225 nm,

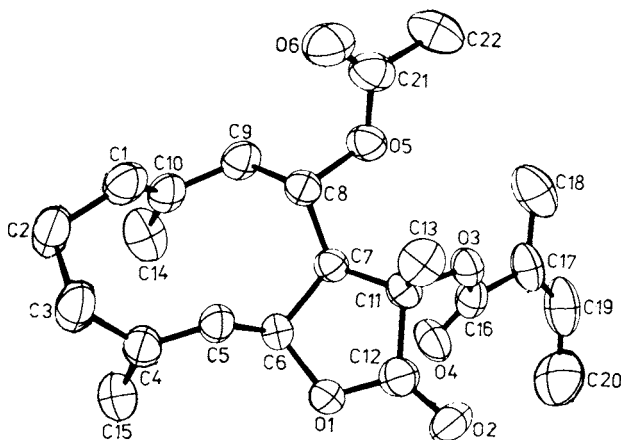


FIG. 1

Perspective drawing of laserolide molecule

$\Delta\epsilon +2.3$) and *XI* (224 nm, $\Delta\epsilon +2.1$) led to the *R*-configuration at the $C_{(11)}$ atom. Thus, the absolute configuration of laserolide is described by the formula *I* and that of isolaserolide (because of its chemical correlation with laserolide³) by the formula *II*.

Laserolide (*I*) is a germacranolide of the ursiniolide type with $6\alpha\text{H}, 7\alpha\text{H}$ -germacra-*(E)1(10), (E)4*-dien-6,12-olide skeleton of (*7S*)-configuration. First compounds of this type, described by us^{13,14}, were ursiniolides A, B and C (*XIII–XV*) from *Ursinia anthemoides* (L.) POIRET. species (*Compositae* family, tribe *Anthemidae*). Laserolide (*I*) is thus the first described germacranolide in the *Umbelliferae* family and, moreover, germacranolide of the ursiniolide type. Isolaserolide (*II*) is a representative of a novel, hitherto undescribed, stereostructural group of elemanolides that can be characterized by sesquiterpenic skeleton $5\beta\text{H}, 6\alpha\text{H}, 7\alpha\text{H}, 10\alpha\text{CH}_3$ -elma-1,3-dien-6,12-olide of (*7S*)-configuration.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Silica gel for the column chromatography was prepared according to Pitra and Štěrba (30– ϵ 0 m μ ; deactivated by 11% water), thin-layer chromatography was performed on silica gel G (Merck) according to Stahl. IR Spectra were measured in chloroform on a Perkin-Elmer PE 580 spectrometer, ¹H and ¹³C NMR spectra (200 MHz and 50.3 MHz, respectively) were taken on a Varian XL-200 instrument in deuteriochloroform with tetramethylsilane as internal standard. Chemical shifts and coupling constants of protons were obtained by first order analysis from expanded spectra (2 Hz/cm) using exponential multiplication with gaussian apodization function for resolution enhancement. Mass spectra were measured on an AEI MS 902 spectrometer, optical rotations were determined in methanol on an objective Perkin-Elmer 141 polarimeter.

CD was measured on a Roussel Jouan CD 185 dichrograph. Laserolide^{1,2} (*I*): CD spectrum (nm, $\Delta\epsilon$): 225, -32.8 . Unsaturated diol² *III*: CD spectrum (nm, $\Delta\epsilon$): 195, $+20.0$; 214, -24.2 ; 235, $+0.8$. Diacetate of saponified laserolide² *IV*: CD spectrum (nm, $\Delta\epsilon$): 213, -36.0 . Monoacetate of saponified laserolide² *V*: CD spectrum (nm, $\Delta\epsilon$): 213, -28.9 .

Ketone *VII*

The diol *III* (1.0 g) in pyridine (12 ml) was mixed with a suspension of chromium trioxide (1.0 g). After standing for 16 h at room temperature, the mixture was diluted with water, extracted with ether and the combined ethereal extracts were washed with an aqueous solution of tartaric acid and with water. The usual work-up procedure afforded a mixture of products (500 mg) which was chromatographed on a column of silica gel with benzene-10% ether as eluant to give the product *VII*, m.p. 159°C (diisopropyl ether). IR Spectrum (cm^{-1}): 1768 (γ -lactone), 1708 (ketone), 1641 (double bond), 3455, 3420 (hydroxyl). Mass spectrum (m/z): 264 (*M*), 246 (*M*-18), 236, 202, 187, 177, 159, 121, 111, 85, 43. CD Spectrum (nm, $\Delta\epsilon$): 212, -6.6 ; 241, $+1.1$; 300, $+2.0$. For $\text{C}_{15}\text{H}_{20}\text{O}_4$ (264.3) calculated: 68.15% C, 7.63% H, 0.38% H act.; found: 67.90% C, 7.53% H, 0.42% H act.

Diesters *VIII* and *X*

Laserolide (*I*; 1.56 g) in benzene (100 ml) was mixed with several drops of boron trifluoride etherate and the mixture was worked up as described in the previous paper². The obtained pro-

duct (1.5 g) was chromatographed on a silica gel column (150 g) with benzene as eluant. The first fractions afforded compound *VIII*, m.p. 105–106°C (diisopropyl ether); $[\alpha]_{\text{D}}^{20} - 51.3^{\circ}$ (*c* 0.16). IR Spectrum (cm^{-1}): 1 780 (γ -lactone), 1 738, 1 250 (acetate), 1 714 (α,β -unsaturated ester), 1 652 (double bond). Mass spectrum (*m/z*): 390 (M), 330 (M–60), 290 (M–100), 248, 230 (M–60–100), 215, 187, 174, 159, 145, 119, 107, 83, 55, 43. CD Spectrum (nm, $\Delta\epsilon$): 207, +2.7; 230, –1.9. For $\text{C}_{22}\text{H}_{30}\text{O}_6$ (390.5) calculated: 67.67% C, 7.74% H; found: 67.70% C, 7.77% H. Further fractions gave compound *X*, m.p. 127–129°C (diisopropyl ether) which was shown by IR spectrum and mixture melting point to be identical with the compound described previously². CD Spectrum (nm, $\Delta\epsilon$): 235, –1.9; 205 (last reading), +2.1.

Diol IX

Compound *VIII* (500 mg) in methanol (10 ml) was mixed with 20% methanolic potassium hydroxide (10 ml) and the mixture was set aside at room temperature for 30 h. The usual processing afforded the diol *IX* (320 mg); m.p. 127–128°C (light petroleum, benzene); $[\alpha]_{\text{D}}^{20} - 6.5^{\circ}$ (*c* 0.17). IR Spectrum (cm^{-1}): 3 470, 3 354, 3 154 (hydroxyl), 1 763 (γ -lactone). Mass spectrum (*m/z*): 266 (M), 248 (M–18), 238, 230 (M–18–18), 223, 215, 204, 189, 177, 161, 145, 43. CD Spectrum (nm, $\Delta\epsilon$): 207, +2.7. For $\text{C}_{15}\text{H}_{22}\text{O}_4$ (266.3) calculated: 67.65% C, 8.33% H, 0.76% H act.; found: 67.72% C, 8.15% H, 0.86% H act.

3,5-Dinitrobenzoate of Diol IX

Compound *IX* (80 mg) in benzene (1.0 ml) was mixed with pyridine (0.5 ml) and 3,5-dinitrobenzoyl chloride (65 mg). After standing for 4 h at room temperature, the mixture was processed as usual and the crude product (100 mg) was purified by chromatography on a column of silica gel (3 g) in benzene–5% ether. The obtained 3,5-dinitrobenzoyl derivative *XII* melted at 203–204°C (toluene); $[\alpha]_{\text{D}}^{20} + 11.4^{\circ}$ (*c* 0.28). IR Spectrum (cm^{-1}): 3 430 (hydroxyl), 1 781 (γ -lactone), 1731, 1 290 (ester), 1 646 (double bond), 1 595, 1 625 (aromatic ring), 1 543, 1 342 (nitro group). Mass spectrum (*m/z*): 460 (M), 430, 400, 248 (M–112), 233, 220, 212, 205, 204, 195, 189, 177, 161, 145, 105, 91, 85, 83, 43. CD Spectrum (nm, $\Delta\epsilon$): 215, +11.4. For $\text{C}_{22}\text{H}_{24}\text{NO}_9$ (460.4) calculated: 57.39% C, 5.26% H, 6.09% N, 0.22% H act.; found: 57.62% C, 5.31% H, 5.84% N, 0.31% H act.

Diol XI

Compound *X* (ref.²; 250 mg) in methanol (5 ml) was mixed with 20% methanolic potassium hydroxide (5 ml) and the mixture was set aside for 18 h at room temperature. The usual work-up gave *XI*, m.p. 165–166°C (light petroleum–benzene); $[\alpha]_{\text{D}}^{20} - 64.8^{\circ}$ (*c* 0.13). IR Spectrum (cm^{-1}): 3 500, 3 600 (hydroxyl), 1 765 (γ -lactone), 1 650 (double bond). Mass spectrum (*m/z*): 266 (M), 248 (M–18), 230 (M–18–18), 204, 189, 161, 105, 43. CD Spectrum (nm, $\Delta\epsilon$): 224, +2.1. For $\text{C}_{15}\text{H}_{22}\text{O}_4$ (266.3) calculated: 67.65% C, 8.33% H, 0.76% act.; found: 67.94% C, 8.17% H, 0.77% H act.

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