

MINOR SESQUITERPENIC LACTONES OF  
*Laser trilobum* (L.) BORKH. SPECIES\*

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Six further sesquiterpenic lactones (*V–X*) and one phenylpropane derivative (*XI*) were isolated from the underground parts of *Laser trilobum* species. The structure, including the relative and absolute configuration, of five hitherto undescribed lactones has been elucidated and described by formulae *VI–X*.

In our earlier investigations we isolated five sesquiterpenic lactones, laserolide (*I*), isolaserolide (*II*), lasolide (*III*), trilobolide (*IV*) and isotrilobolide<sup>1</sup>, from the underground parts of *Laser trilobum* (L.) BORKH. species (*Umbelliferae*<sup>5</sup> family, *Laserpitieae* tribe). Recently, we derived the stereostructure (including absolute configuration) for laserolide (*I*)<sup>2,3</sup>, isolaserolide (*II*)<sup>2,3</sup>, lasolide (*III*)<sup>2,4</sup> and trilobolide (*IV*)<sup>2,5</sup>. Compound *IV* was assigned relative configuration also by German authors<sup>6</sup> and absolute configuration by Danish investigators<sup>7</sup>. The present communication which represents the full paper on further, minor lactones from the *L. trilobum* species, appeared earlier in a preliminary form<sup>2</sup>.

Column chromatography on silica gel of light petroleum extract of the above-mentioned species afforded six minor, in this species hitherto undescribed, lactones *V–X*. The phenylpropane derivative *XI* was obtained from the chloroform extract. One of the lactones, 2 $\beta$ -angeloyloxy-8 $\alpha$ -(2'-methyl)butyryloxy-10 $\beta$ ,11 $\alpha$ -diacetoxyslov-3-enolide (*V*), was found already previously in underground parts of *L. archangelica* WULF. species<sup>8</sup> and its structure was derived on the basis of chemical as well as <sup>1</sup>H NMR spectral correlation with 8 $\alpha$ -angeloyloxy-10 $\beta$ ,11 $\alpha$ -diacetoxyslov-3-enolide (*XII*)<sup>8,9</sup>. We have found now that the originally published values of melting point (69–71°C) and optical rotation ( $[\alpha]_D^{20} + 35.8^\circ$ ) of compound *V* (archangelolide)<sup>8</sup> are too low and are actually 109–112°C and  $-120.2^\circ$ , respectively.

The least polar compound *VI* had m.p. 105–107°C,  $[\alpha]_D^{20} - 138.6^\circ$  and composition C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>. According to the IR spectrum, it contained a  $\gamma$ -lactone grouping (1 775 cm<sup>-1</sup>) and an  $\alpha,\beta$ -unsaturated ester group (1 710 and 1 645 cm<sup>-1</sup>). Its mass

\* Part CCXCI in the series On Terpenes; Part CCXC: Acta Entomol. Bohemosl., in press.

spectrum exhibited molecular peak at  $m/z$  332 and characteristic signals at 232 ( $M-100$ ), 83 ( $C_4H_7CO^+$ ) and 55 ( $C_4H_7^+$ ). The CD spectrum showed highest value at 223 nm ( $\Delta\epsilon -29.2$ ; last reading). Comparison of these data and the  $^1H$  and  $^{13}C$  NMR parameters with those of laserolide (*I*)<sup>3</sup> (Tables I and II) has shown that the compound must have the structure *VI* (including the absolute configuration) and hence is 8-deacetylaserolide.

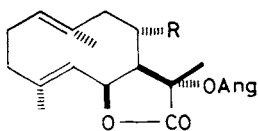
TABLE I

Proton and carbon-13 NMR data of compounds *VI* and *I* in deuteriochloroform

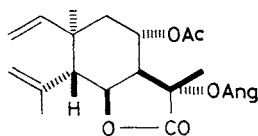
Proton	$^1H$ -NMR ( $J_{H,H}$ )		Carbon	$^{13}C$ -NMR	
	<i>VI</i>	<i>I</i>		<i>VI</i>	<i>I</i>
H-1	4.93 m (9.9; 6.2; 1.7; 1.5 (3×))	5.11 m	C (1)	125.89	128.48
H-2			C (2)	25.15	25.64
H-2'	1.59—2.22	1.90—2.40	C (3)	39.86	39.40
H-3			C (4)	140.84	142.99
H-3'			C (5)	122.66	122.08
H-5	4.79 dm (10.6; 1.5 (3×); ≠0)	4.74 dm (10.3; 1.5 (3×); ≠0)	C (6)	76.21	73.52
H-6	5.43 dd (10.6; 8.9)	5.38 dd (10.3; 9.4)	C (7)	44.86	46.75
H-7	3.11 ddd (9.7; 8.9; 3.8)	3.72 dd (11.3; 9.4)	C (8)	27.35	73.49
H-8		5.28 ddd (11.3; 10.8; 4.0)	C (9)	35.81	41.91
H-8'	1.59—2.22	—	C (10)	138.52	133.57
H-9		2.86 bd (14.0; ≠0)	C (11)	80.80	79.38
H-9'		1.84 dd (14.0; 10.8)	C (12)	175.09	174.28
H-13	1.54 s	1.52 s	C (13)	19.70	19.72
H-14	1.41 d (1.5)	1.40 bd (1.3; ≠0)	C (14)	17.12	17.45
H-15	1.73 d (1.5)	1.74 d (1.5)	C (15)	20.64	20.88
<sup>a</sup>	—	2.07 s	C (1') <sup>a</sup>	—	169.97
<sup>b</sup>	6.18 qq (7.2 (3×); 1.5 (3×))	6.20 qq (7.3 (3×); 1.5 (3×))	C (2') <sup>a</sup>	—	21.23
<sup>b</sup>	1.91 p (1.5 (4×))	1.93 p (1.5 (4×))	C (1') <sup>b</sup>	166.43	166.37
<sup>b</sup>	2.01 dq (7.2; 1.5 (3×))	2.04 dq (7.3; 1.5 (3×))	C (2') <sup>b</sup>	126.85	126.65
			C (3') <sup>b</sup>	140.19	140.67
			C (4') <sup>b</sup>	15.82	15.87
			C (5') <sup>b</sup>	20.24	20.23

<sup>a</sup> O-Acetyl; <sup>b</sup> O-angeloyl.

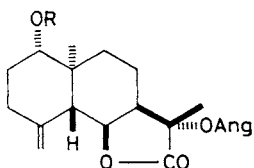
Compound VII, more polar than VI, had m.p. 126–127°C,  $[\alpha]_D^{20} -94.6^\circ$ , and composition  $C_{24}H_{34}O_8$ . Its IR spectrum showed the presence of a  $\gamma$ -lactone grouping ( $1784\text{ cm}^{-1}$ ), an acetate group ( $1732, 1250\text{ cm}^{-1}$ ) and a double bond ( $1649\text{ cm}^{-1}$ ). Mass spectrum displayed characteristic peaks at  $m/z$  390 ( $M-60$ ), 330 ( $M-60-60$ ), 228 ( $M-60-60-102$ ), 85 ( $C_4H_9CO^+$ ) and 57 ( $C_4H_9^+$ ). The highest CD value was



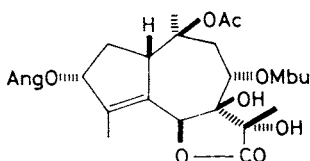
I, R = OAc  
VI, R = H



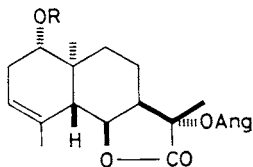
II



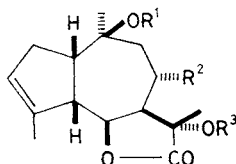
III, R = H  
XIX, R = TAC



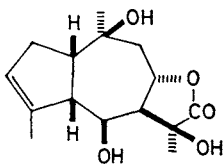
IV



X, R = H  
XVIII, R = TAC



VII,  $R^1, R^3 = \text{Ac}$ ;  $R^2 = \text{OMbu}$   
VIII,  $R^1, R^2 = \text{H}$ ;  $R^3 = \text{Ang}$   
XII,  $R^1, R^3 = \text{Ac}$ ;  $R^2 = \text{OAng}$   
XIV,  $R^1 = \text{TAC}$ ;  $R^2 = \text{H}$ ;  $R^3 = \text{Ang}$   
XV,  $R^1 = \text{H}$ ;  $R^2 = \text{OAng}$ ;  $R^3 = \text{Ac}$   
XVI,  $R^1 = \text{TAC}$ ;  $R^2 = \text{OAng}$ ;  $R^3 = \text{Ac}$



XIII

TABLE II  
CD spectra and  $[\alpha]_D^{20}$  of sesquiterpenic lactones *I*, *III*, *V–X*, *XII*, and *XV*

Compound	<i>I</i>	<i>VI</i>	<i>XII</i>	<i>VII</i>	<i>XV</i>	<i>VIII</i>	<i>V</i>	<i>IX</i>	<i>III</i>	<i>X</i>
$\lambda$ , nm	225	223 <sup>a</sup>	210 <sup>a</sup>	210 <sup>a</sup>	210 <sup>a</sup>	210 <sup>a</sup>	205 <sup>a</sup>	210 <sup>a</sup>	230	227
$\Delta\epsilon$	-32.8	-29.2	-4.1	-3.1	-3.6	-4.3	-12.1	-11.9	-2.2	-4.0
$[\alpha]_D^{20}$	-234.0	-138.6	-78.2	-94.6	-25.2	-126.0	-120.2	-66.4	-90.7	-62.3

<sup>a</sup> Last reading.

TABLE III  
Proton and carbon-13 NMR data of compounds *VII* and *XII* in deuteriochloroform

Proton	<sup>1</sup> H-NMR ( $J_{H,H}$ )		Carbon	<sup>13</sup> C-NMR	
	<i>VII</i>	<i>XII</i>		<i>VII</i>	<i>XII</i>
H-1	2.73 m (10.9; 7.1; 5.8; 1.6)	2.77 m (11.5; 7.2; 5.8; 1.4)	C (1)	53.72	53.48
H-2	2.10–2.30	2.30 m (15.4; 7.2; 3.1; 1.6 (3×))	C (2)	31.59	31.30
H-2'		2.16 m (15.4; 11.5; 2.2 (3×); 1.6)	C (3)	125.51	125.46
H-3	5.57 m (3.0; 1.7 (3×); 1.5)	5.57 m (3.1; 1.7 (3×); 1.6)	C (4)	146.17	145.63
H-5	2.56 dd (11.6; 5.8)	2.60 dd (11.6; 5.8)	C (5)	49.04	48.76
H-6	4.72 dd (11.6; 9.9)	4.74 dd (11.6; 9.9)	C (6)	77.55	77.39
H-7	3.62 dd (11.0; 9.9)	3.67 dd (11.1; 9.9)	C (7)	47.81	47.47
H-8	5.59 ddd (11.0; 10.1; 0.9)	5.67 ddd (11.1; 10.1; 1.1)	C (8)	64.16	63.87
H-9	2.59 ddd (15.0; 1.6; 0.9)	2.67 ddd (15.1; 1.4; 1.1)	C (9)	40.79	40.33
H-9'	1.95 dd (15.0; 10.1)	2.01 dd (15.1; 10.1)	C (10)	82.53	82.49
H-13	1.53 s	1.59 s	C (11)	78.21	77.96
H-14	1.56 s	1.54 s	C (12)	173.85	173.61
H-15'	1.89 m (2.2; 1.7 (2×))	1.90 m (2.2; 1.7; 1.6)	C (13)	20.17	19.91
<sup>a</sup>	2.10 s	2.13 s	C (14)	24.59	24.36
	2.06 s	2.02 s	C (15)	18.51	18.21
<sup>b</sup>	2.31 m (6.4; 7.8; 6.9 (3×))	—	C (1') <sup>a</sup>	170.22	169.95
			C (2') <sup>a</sup>	169.49	169.10
				20.83	20.43
				22.53	22.29

TABLE III  
 (Continued)

Proton	$^1\text{H-NMR } (J_{\text{H,H}})$		Carbon	$^{13}\text{C-NMR}$	
	<i>VII</i>	<i>XII</i>		<i>VII</i>	<i>XII</i>
<i>b</i>	1.71 m (13.4; 7.8; 7.4 (3×))	—	C (1') <sup>b</sup>	174.83	—
<i>b</i>	1.45 m (13.4; 6.4; 7.4 (3×))	—	C (2') <sup>b</sup>	41.32	—
<i>b</i>	1.15 d (6.9)	—	C (3') <sup>b</sup>	26.40	—
<i>b</i>	0.94 t (7.4 (2×))	—	C (4') <sup>b</sup> C (5') <sup>b</sup>	11.61 16.39	—
<i>c</i>	—	6.09 qq (7.3 (3×); 1.5 (3×))	C (1') <sup>c</sup>	—	165.76
<i>c</i>	—	1.86 p (1.5 (4×))	C (2') <sup>c</sup> C (3') <sup>c</sup>	—	127.09 138.10
<i>c</i>	—	1.99 dq (7.3; 1.5 (3×))	C (4') <sup>c</sup> C (5') <sup>c</sup>	—	15.31 19.91

<sup>a</sup> O-Acetyl; <sup>b</sup> O-2-methylbutyryl; <sup>c</sup> O-angeloyl.

observed at 210 nm ( $\Delta\epsilon -3.1$ ). These data and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, their comparison with analogous values, particularly for  $8\alpha$ -angeloyloxy- $10\beta$ , $11\alpha$ -diacetoxylov-3-enolide (*XII*) (Table II and III), and a direct chemical correlation of compound *VII* with *XII* via the identical hydrolysis product (the trihydroxy lactone *XIII*) led to the conclusion that the compound is  $8\alpha$ -(2'-methyl)butyryloxy- $10\beta$ , $11\alpha$ -diacetoxylov-3-enolide whose absolute configuration can be expressed by formula *VII*.

Further elution gave compound *VIII*, m.p. 186–189°C,  $[\alpha]_{\text{D}}^{20} -126.0^\circ$ , composition  $\text{C}_{20}\text{H}_{28}\text{O}_5$ . Its IR spectrum displayed bands due to a hydroxyl (3 610 and 3 530  $\text{cm}^{-1}$ ), a  $\gamma$ -lactone (1 769  $\text{cm}^{-1}$ ) and an  $\alpha,\beta$ -unsaturated ester (1 710 and 1 645  $\text{cm}^{-1}$ ). The mass spectrum contained a molecular peak at  $m/z$  348 and characteristic signals at  $m/z$  330 ( $\text{M}-18$ ), 248 ( $\text{M}-100$ ), 230 ( $\text{M}-18-100$ ), 83 ( $\text{C}_4\text{H}_7\text{CO}^+$ ) and 55 ( $\text{C}_4\text{H}_7^+$ ). In the CD spectrum, the highest value of  $\Delta\epsilon -4.3$  was found at 210 nm (last reading). Comparison of  $^1\text{H}$  and  $^{13}\text{C}$  NMR parameters of *VIII* and its TAC derivative *XIV* with those of  $8\alpha$ -angeloyloxy- $10\beta$ -hydroxy- $11\alpha$ -acetoxylov-3-enolide (*XV*) and its TAC derivative *XVI* (Tables II and IV) revealed that the studied compound is  $10\beta$ -hydroxy- $11\alpha$ -angeloyloxylov-3-enolide whose absolute configuration is given by formula *VIII*.

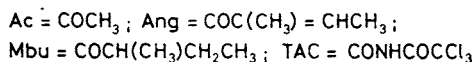
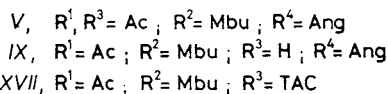
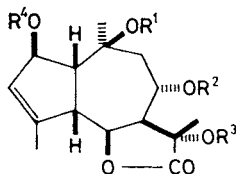
TABLE IV  
Proton and carbon-13 NMR data of compounds VIII, XIV–XVI in deuteriochloroform

Proton	<sup>1</sup> H-NMR ( <i>J</i> <sub>H,H</sub> )				Carbon	<sup>13</sup> C-NMR			
	VIII	XIV	XV	XVI		VIII	XIV	XV	XVI
H-1	—	—	2.43 m (11.5; 6.9; 5.5; 1.7)	2.95	C (1)	51.27	50.88	56.01	53.05
H-2	2.31–2.64	2.36–3.15	2.22 m (15.1; 6.9; 3.2; 1.4 (3×))	2.19	C (2)	33.49	33.23	32.23	31.95
H-2'	—	—	2.08 m (15.1; 11.5; 2.3 (3×); 1.6)	2.34	C (3)	125.76	126.04	125.91	125.30
H-3	5.49 m (1.5 (3×); 1.4 (2×))	5.54	5.55 m (3.2; 1.7 (3×); 1.6)	5.59	C (4)	142.28	141.46	147.10	146.57
H-5	2.79 m	2.36–3.15	2.58 bdd (11.6; 5.5)	2.71	C (5)	49.52	51.32	49.36	48.86
H-6	5.39 dd (11.8; 9.3)	5.23	4.72 dd (11.6; 9.9)	4.74	C (6)	82.79	81.93	78.30	77.37
H-7	3.23 m	2.36–3.15	3.67 dd (11.5; 9.9)	3.67	C (7)	42.37	42.33	47.48	47.59
H-8	—	—	5.54 ddd (11.5; 9.2; 1.0)	5.66	C (8)	21.88	21.09	66.94	64.22
H-8'	1.73–2.0	1.80–2.05	—	—	C (9)	40.15	33.53	43.60	41.91
H-9	—	—	2.04 dd (14.8; 9.2; 1.7)	2.48	C (10)	73.11	89.20	71.33	86.87
H-9'	—	—	1.81 dd (14.8; 1.0)	2.07	C (11)	76.69	79.39	78.53	78.27
H-13	1.49 s	1.48	1.55 s	1.53	C (12)	175.67	175.46	174.14	173.78
					C (13)	20.38	20.08	20.19	20.04
					C (14)	32.16	26.94	31.10	24.93
					C (15)	18.35	18.27	18.85	18.64
					C (1) <sup>a</sup>	—	—	169.72	169.68
					C (2) <sup>a</sup>	—	—	20.98	20.83
					C (1) <sup>b</sup>	166.47	166.64	167.23	166.03
					C (2) <sup>b</sup>	126.93	126.61	127.09	126.79
					C (3) <sup>b</sup>	140.20	140.66	140.70	140.40
					C (4) <sup>b</sup>	15.98	16.03	15.98	15.82
					C (5) <sup>b</sup>	20.28	20.31	20.42	20.16

H-14	1.19 s	1.65	1.23 s	1.67
H-15	1.86 m	1.87	1.89 m	1.91
	(2.4; 1.6 (2×))	—	(2.3; 1.7; 1.4)	
<sup>a</sup>	—	—	2.06 s	2.04
<sup>b</sup>	6.15 qq	6.14	6.21 qq	6.15
	(7.2 (3×); 1.5 (3×))	—	(7.3 (3×); 1.5 (3×))	
<sup>b</sup>	1.88 p	1.84	1.89 p	1.86
	(1.5 (4×))	—	(1.5 (4×))	
<sup>b</sup>	1.99 dq	1.94	2.05 dq	1.99
	(7.3; 1.5 (3×))	—	(7.3; 1.5 (3×))	
NH	—	8.52	—	8.45

<sup>a</sup> O-Acetyl; <sup>b</sup> O-angeloyl.

The chromatographic separation afforded further a noncrystalline compound *IX*,  $[\alpha]_D^{20} -66.4^\circ$  of composition  $C_{27}H_{38}O_9$ . According to the IR spectrum, it contained a hydroxyl ( $3\,570$  and  $3\,470\text{ cm}^{-1}$ ), a  $\gamma$ -lactone ( $1\,784\text{ cm}^{-1}$ ), an ester ( $1\,730\text{ cm}^{-1}$ ) and a double bond ( $1\,652\text{ cm}^{-1}$ ). No molecular peak was observed in the mass



spectrum, which showed characteristic fragments at  $m/z$  446 ( $M-60$ ), 428 ( $M-60-18$ ), 346 ( $M-60-100$ ), 244 ( $M-60-100-102$ ), 85 ( $C_4H_9CO^+$ ), 83 ( $C_4H_7\cdot CO^+$ ), 57 ( $C_4H_9^+$ ) and 55 ( $C_4H_7^+$ ). A CD maximum was found at 210 nm ( $\Delta\epsilon -11.9$ ). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral parameters of the compound and its TAC derivative *XVII* are given in Table V. The structure and absolute configuration of *IX* follows from comparison of its spectral parameters (Table II and V) with those of 2 $\beta$ -angeloyloxy-8 $\alpha$ -(2'-methyl)-butyryloxy-10 $\beta$ ,11 $\alpha$ -diacetoxyslov-3-enolide (*V*), as well as from their chemical correlation: compound *IX* is 2 $\beta$ -angeloyloxy-8 $\alpha$ -(2'-methyl)-butyryloxy-10 $\beta$ -acetoxy-11 $\alpha$ -hydroxyslov-3-enolide.

The chromatography gave then a more polar compound *X*, m.p. 120–121°C,  $[\alpha]_D^{20} -62.3^\circ$ , of composition  $C_{20}H_{28}O_5$ . Its IR spectrum revealed the presence of a hydroxyl ( $3\,615$  and  $3\,525\text{ cm}^{-1}$ ), a  $\gamma$ -lactone ( $1\,780\text{ cm}^{-1}$ ), an  $\alpha,\beta$ -unsaturated ester ( $1\,712\text{ cm}^{-1}$ ) and a double bond ( $1\,644\text{ cm}^{-1}$ ). A molecular peak at  $m/z$  348 was observed in the mass spectrum, along with ions at  $m/z$  248 ( $M-100$ ), 230 ( $M-100-18$ ), 83 ( $C_4H_7CO^+$ ) and 55 ( $C_4H_7^+$ ). The highest CD value was observed at 227 nm ( $\Delta\epsilon -4.0$ ).

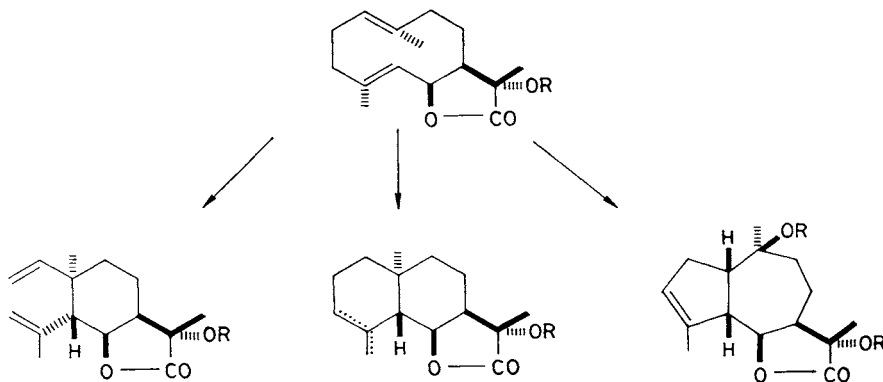
These data, together with the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound *X* and its TAC derivative *XVIII*, were compared with the analogous parameters of lasolide (*III*) and its TAC derivative *XIX* (Table II and VI), showing its structure and absolute configuration to be represented by formula X. For this natural lactone we suggest the name isolasolide.

We isolated also lasolide (*III*), which had been found in this material already earlier<sup>1</sup>, corrected its originally published melting point from 149–151°C to 166–



169°C, determined its rotation ( $[\alpha]_D^{20} -90.8$ ) and measured its CD spectrum which displayed Cotton effect at 230 nm ( $\Delta\epsilon -2.2$ ).

The chloroform extract from roots of *L. trilobum* afforded, in addition to the compounds already found in the light petroleum extract and a considerable amount of trilobolide (*IV*)<sup>1</sup>, also 1-(3,4-methylenedioxy-5-hydroxyphenyl)propan-1-one (*XI*), m.p. 160–162°C, which was identified by its mass and IR spectra and by mixture melting point with an authentic sample<sup>10</sup>.



SCHEME 1

As follows from the structures of the sesquiterpene lactones from the *L. trilobum* species, all these natural compounds belong to the fundamental sesquiterpene types — germacranolides, guaianolides, eudesmanolides and elemanolides — that contain a  $\gamma$ -lactone ring *cis*-annulated to the corresponding homocycle and differ in the stereostructure from the analogous types, characteristic of the sesquiterpene lactones of the *Compositae* family species. The stereostructure of the described lactones lends support to the assumption that part of their biogenesis proceeds as depicted in Scheme 1. This scheme is analogous to, but stereostructurally different from, the supposed scheme of biogenesis of typical sesquiterpene lactones of the *Compositae* family.

As concerns trilobolide (*IV*), its absolute configuration at the C(7)—C(11) bond differs from the configuration of most of the so far described sesquiterpene lactones from both the *Compositae* and *Umbelliferae* families. However, many characteristic structural features of trilobolide (*e.g.* the  $1\beta\text{H}$ ,  $6\alpha\text{H}$ ,  $8\beta\text{H}$ ,  $10\alpha\text{CH}_3$  and  $10\beta\text{OCOCH}_3$  configuration) prove its close relation with lactones of the slovanolide type. We assume therefore that biogenesis of the lactone part of its molecule could start from a slovanolide-type precursor as *e.g.* shown in Scheme 2. The assumed intermediate *XX* of this biogenesis has its analogy in the structure of 8-deangeloylshairidin (*XXI*) and

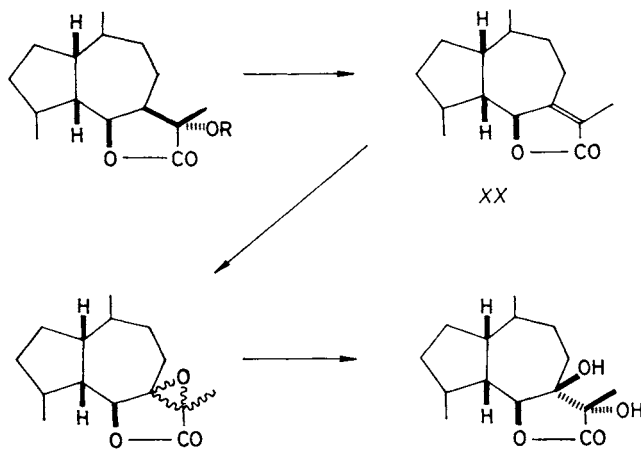
TABLE V  
Proton and carbon-13 NMR data of compounds IX, XVII, and V in deuteriochloroform

Proton	<sup>1</sup> H-NMR ( <i>J</i> <sub>H,H</sub> )			Carbon	<sup>13</sup> C-NMR		
	IX	XVII	V		IX	XVII	V
H-1	3·29 dd (7·5; 3·9)	3·38	3·32 dd (7·9; 3·5)	C (1)	52·96	52·36	52·65
H-2	5·80 m	5·83	5·83 m	C (2)	78·65	78·81	78·76
H-3	5·66 m	5·68	(3·5; 2·4; 1·4; 1·2 (3×))	C (3)	126·97	127·14	126·87
H-5	3·07 m	3·06	(2·4; 1·8; 1·5 (3×))	C (4)	148·77	148·56	148·77
H-6	4·64 dd (11·8; 9·3)	4·92	(11·9; 7·9; 1·8; 1·4)	C (5)	49·30	49·87	49·85
H-7	3·04 dd (10·5; 9·3)	3·82	3·05 m	C (6)	77·35	76·94	76·68
H-8	5·70 dt (11·1; 10·5; 2·2)	5·69	4·82 dd (11·9; 9·7)	C (7)	53·25	47·99	47·91
H-9	2·59 dd (15·5; 2·2)	2·58	3·62 dd (11·2; 9·7)	C (8)	64·76	65·03	65·17
H-9'	2·12 dd (15·5; 11·1)	2·15	5·62 df (11·2; 10·9; 2·6)	C (9)	43·60	43·77	43·78
H-13	1·58 s	1·67	2·60 dd (15·2; 2·6)	C (10)	81·11	80·76	80·78
H-14	1·43 s	1·43	2·06 dd (15·2; 10·9)	C (11)	73·24	80·67	77·95
H-15	1·92	1·95	1·58 s	C (12)	178·58	172·37	173·36
			1·43 s	C (13)	22·42	20·26	20·17
			1·95 dd (1·5; 1·2)	C (14)	26·45	26·40	26·02
				C (15)	17·44	17·44	17·45
				C (1') <sup>a</sup>	170·12	170·01	169·82
				C (2') <sup>a</sup>	22·27	22·18	22·10
				C (1') <sup>b</sup>	175·20	174·61	174·56
				C (2') <sup>b</sup>	41·80	41·07	41·10
				C (3') <sup>b</sup>	26·25	26·21	26·19

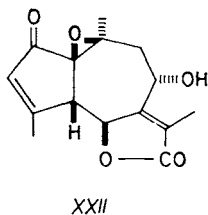
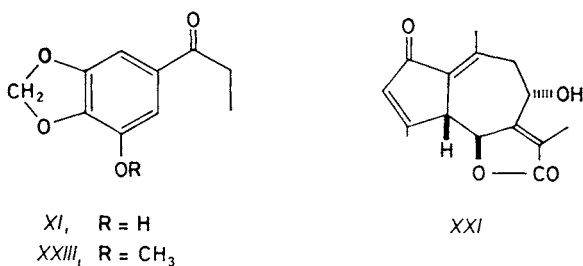
a	2.05 s	2.03	2.08 s	C (4) <sup>b</sup>	11.50	11.55	11.44
b	2.36 m (7.0 (5×))	2.33	2.02 s	C (5) <sup>b</sup>	16.25	16.15	16.15
b	1.73 m	1.69	2.33 m	C (1) <sup>c</sup>	167.42	167.21	167.15
b	1.45 m	1.43	(7.6; 6.9 (3×); 6.4)	C (2) <sup>c</sup>	127.62	127.63	127.57
b	1.18 d (7.0)	1.12	1.72 m	C (3) <sup>c</sup>	137.96	137.71	137.56
b	0.91 t	0.91	(13.6; 7.4 (3×); 6.4)	C (4) <sup>c</sup>	15.65	15.60	15.48
c	(7.4 (2×))	6.04	(13.6; 7.6; 7.4 (3×))	C (5) <sup>c</sup>	20.43	20.39	20.29
c	6.05 qq (7.2 (3×); 1.5 (3×))	1.86	1.15 d (6.9)				
c	1.86 p (1.5 (4×))	1.95	0.93 t				
c	1.95 dq (7.2; 1.5 (3×))	8.67	(7.4 (2×))				
NH	—	—	6.05 qq (7.2 (3×); 1.5 (3×))				
	—	—	1.87 p				
	—	—	(1.5 (4×))				
	—	—	1.95 dq				
	—	—	(7.2; 1.5 (3×))				

<sup>a</sup> O-acetyl; <sup>b</sup> O-2-methylbutyryl; <sup>c</sup> O-angeloyl.

guillonein (XXII), obtained from *Guillonea scabra* CAV. COSSON species (*Umbelliferae* family, *Laserpitieae* tribe)<sup>11-14</sup>.



SCHEME 2



### EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Column chromatography was carried out on silica gel according to Pitra and Štěrba (30  $\mu$ , deactivated with 11% water). Infrared spectra were recorded in chloroform on a Perkin-Elmer 580 spectrometer, NMR spectra

TABLE VI  
Proton and carbon-13 NMR data of compounds X, XVIII, III, and XIX in deuteriochloroform

Proton	<sup>1</sup> H-NMR ( <i>J</i> <sub>H,H'</sub> )			Carbon	<sup>13</sup> C-NMR				
	X	XVIII	III		XIX	X	XVIII	III	XIX
H-1	3·57 dd (9·8; 6·4)	4·89	3·44 bd (11·0; ≠0)	4·78	C (1)	74·84	80·20	77·92	83·64
H-2	2·34 m (17·2; 6·4; 1·5 (5×))	2·55	1·40—2·11	—	C (2)	21·29	28·44	31·18	27·48
H-2'	1·40—2·13	1·39—2·27	—	1·40—2·20	C (3)	121·79	120·54	32·53	32·08
H-3	5·39 m	5·41	2·40 m	2·47	C (4)	133·01	133·31	142·57	141·17
H-3'	—	—	1·40—2·11	1·40—2·20	C (5)	47·38	47·21	49·31	49·23
H-5	1·40—2·13	1·39—2·27	—	—	C (6)	78·30	77·34	75·12	74·38
H-6	4·82 dd (10·9; 9·0)	4·82	5·03 dd (11·0; 9·3)	5·03	C (7)	38·86	38·43	37·60	37·29
H-7	3·26 m (9·0; 7·2; 5·6)	3·29	3·34 m (9·3; 4·7 (2×))	3·38	C (8)	18·48	18·07	18·04	17·22
H-8	—	—	—	—	C (9)	32·04	31·04	33·96	33·37
H-8'	1·40—2·13	1·39—2·27	1·40—2·11	1·40—2·20	C (10)	37·34	36·53	40·04	39·32
H-9	—	—	—	—	C (11)	79·94	79·53	79·54	79·26
H-9'	—	—	—	—	C (12)	174·70	174·16	174·92	174·50
H-13	1·59 s	1·59	1·61 s	1·61	C (13)	19·84	19·81	20·65	20·61
H-14	0·84 s	0·99	0·75 s	0·91	C (14)	11·52	12·42	11·15	11·11
H-15	1·87 m (2·5; 1·3 (2×))	1·89	5·05 b 4·95 b	5·11	C (15)	22·41	22·45	110·04	111·15
<sup>a</sup>	6·17 qq (7·3 (3×); 1·5 (3×))	6·17	6·17 qq (7·3 (3×); 1·5 (3×))	6·17	C (1') <sup>a</sup>	166·20	165·97	166·27	166·17
<sup>a</sup>	1·89 p (1·5 (4×))	1·89	1·89 p (1·5 (4×))	1·89	C (2') <sup>a</sup>	126·78	126·68	126·82	126·75
<sup>a</sup>	2·00 dq (7·3; 1·5 (3×))	1·99	2·00 dq (7·3; 1·5 (3×))	2·00	C (3') <sup>a</sup>	140·21	140·16	140·33	140·46
NH	—	8·38	—	8·33	C (4') <sup>a</sup>	15·79	15·69	15·87	15·84
					C (5') <sup>a</sup>	20·22	20·11	20·25	20·22

<sup>a</sup> O-Angeloyl.

were obtained on a Varian XL-200 instrument ( $^1\text{H}$  at 200 MHz,  $^{13}\text{C}$  at 50-31 MHz) in deuteriochloroform with tetramethylsilane as internal standard. The *in situ* acylations were performed by adding slight excess of trichloroacetyl isocyanate (TAI) into solution of the compound in the NMR tube. The NMR data are summarized in Tables I, III–VI. The signal multiplicities and coupling constants for derivatives XIV, XVI–XIX are almost the same before and after acylation with TAI and therefore the data for the acyl derivatives are not given in the Tables. Mass spectra were measured on an AEI MS 902 spectrometer, optical rotations were determined in methanol on a Perkin-Elmer 141 objective polarimeter. CD spectra were taken on a Roussel Jouan CD 185 dichrographe in methanol.

#### Isolation of the Components

A part (100 g) of light petroleum extract from roots and rhizomes of *Laser trilobum* (L.) BORKH. species<sup>1</sup> was chromatographed on a column of silica gel (1 000 g). The material was eluted first with toluene and then toluene with increasing content of ether. Some of the nine fractions obtained were processed further (Table VII). The chromatographic separation was followed by thin-layer chromatography on silica gel.

#### 8-Deacetylaserolide (VI)

Crystallization of fraction 3 (Table VII) afforded compound VI (253 mg), m.p. 105–107°C (light petroleum). IR spectrum ( $\text{cm}^{-1}$ ): 1 775 ( $\gamma$ -lactone), 1 645 ( $\alpha,\beta$ -unsaturated ester). Mass spectrum ( $m/z$ ): 332 (M), 232 (M–100), 83 ( $\text{C}_4\text{H}_7\text{CO}^+$ ), 55 ( $\text{C}_4\text{H}_7^+$ ). For  $\text{C}_{20}\text{H}_{28}\text{O}_4$  (332.4) calculated: 72.27% C, 8.49% H; found: 72.42% C, 8.41% H.

#### 8 $\alpha$ -(2'-Methyl)butyryloxy-10 $\beta$ ,11 $\alpha$ -diacetoxy-3-enolide (VII)

Crystallization of fraction 5 (Table VII) gave compound VII (1.0 g), m.p. 126–127°C (light petroleum). IR spectrum ( $\text{cm}^{-1}$ ): 1 784 ( $\gamma$ -lactone), 1 732, 1 250 (acetate), 1 649 (double bond). Mass spectrum ( $m/z$ ): 390 (M–60), 330 (M–60–60), 228 (M–60–60–102), 85 ( $\text{C}_4\text{H}_9\text{CO}^+$ ), 57 ( $\text{C}_4\text{H}_9^+$ ). For  $\text{C}_{24}\text{H}_{34}\text{O}_8$  (450.5) calculated: 63.99% C, 7.61% H; found: 64.02% C, 7.78% H.

TABLE VII

Chromatography of light petroleum extract from the underground parts of *L. trilobum*

Fraction	Solvent	Weight, g	Compounds
1	Toluene	38.2	—
2	Toluene	8.1	XXIII
3	Toluene	3.2	VI
4	Toluene + 5% ether	5.4	II
5	Toluene + 10% ether	10.1	I, VII
6	Toluene + 20% ether	4.6	V, VIII
7	Toluene + 50% ether	4.7	IX, X
8	Toluene + 50% ether	5.0	III
9	Ether	1.5	—

Trihydroxy Lactone *XIII*

A solution of compound *VII* (100 mg) in methanol (5 ml) was mixed with 33% methanolic potassium hydroxide (15 ml) and the mixture was set aside for 24 h at room temperature with intermittent stirring. Water (20 ml) was added and most of the methanol was removed *in vacuo*. The aqueous solution was acidified with 5% sulfuric acid, extracted with ether, the combined ethereal extracts were washed with aqueous sodium hydrogen carbonate and water and dried over sodium sulfate. Removal of the solvent afforded the trihydroxy lactone *XIII* (32 mg), m.p. 192 to 194°C (diisopropyl ether), identical with an authentic specimen<sup>15</sup> (IR, CD, <sup>1</sup>H NMR spectra and mixture melting point).

2β-Angeloyloxy-8α-(2'-methyl)butyryloxy-10β,11α-diacetoxyslov-3-enolide (*V*)

Repeated column chromatography of fraction 6 (Table VII) on silica gel afforded *V* (56 mg), m.p. 109–112°C (light petroleum), composition C<sub>29</sub>H<sub>40</sub>O<sub>10</sub>. Its identity with an authentic sample<sup>8</sup> was proved by comparison of the mass, IR and <sup>1</sup>H NMR spectra and by mixture melting point determination.

10β-Hydroxy-11α-angeloyloxyslov-3-enolide (*VIII*)

Repeated chromatography of fraction 6 (Table VII) afforded *VIII* (30 mg), m.p. 186–189°C (light petroleum). IR spectrum (cm<sup>-1</sup>): 3 610, 3 530 (hydroxyl), 1 769 (γ-lactone), 1 710, 1 645 (α,β-unsaturated ester). Mass spectrum (*m/z*): 348 (M), 330 (M-18), 248 (M-100), 230 (M-18-100), 83 (C<sub>4</sub>H<sub>7</sub>CO<sup>+</sup>), 55 (C<sub>4</sub>H<sub>7</sub><sup>+</sup>). For C<sub>20</sub>H<sub>28</sub>O<sub>5</sub> (348.4) calculated: 68.95% C, 8.10% H, 0.29% H act.; found: 69.09% C, 8.38% H, 0.30% H act.

2β-Angeloyloxy-8α-(2'-methyl)butyryloxy-10β-acetoxy-11α-hydroxyslov-3-enolide (*IX*)

Repeated chromatography of fraction 7 (Table VII) on a silica gel column gave noncrystalline compound *IX* (1.4 g). IR spectrum (cm<sup>-1</sup>): 3 570, 3 470 (hydroxyl), 1 784 (γ-lactone), 1 730 (ester), 1 652 (double bond). Mass spectrum (*m/z*): 446 (M-60), 428 (M-60-18), 346 (M-60-

TABLE VIII

Chromatography of chloroform extract from the underground parts of *L. trilobum*

Fraction		Weight, g	Compounds
1	Light petroleum + 10% ether	4.4	—
2	Light petroleum + 20% ether	1.5	<i>XXIII</i>
3	Light petroleum + 30% ether	0.9	—
4	Light petroleum + 35% ether	2.3	<i>I, II</i>
5	Light petroleum + 40% ether	3.0	<i>XI</i>
6	Light petroleum + 50% ether	2.7	—
7	Ether	4.3	—
8	Ether	45.5	<i>IV</i>
9	Ether + 5% methanol	18.5	—

100), 244 (M-60-100-102), 85 (C<sub>4</sub>H<sub>9</sub>CO<sup>+</sup>), 83 (C<sub>4</sub>H<sub>7</sub>CO<sup>+</sup>), 57 (C<sub>4</sub>H<sub>9</sub><sup>+</sup>), 55 (C<sub>4</sub>H<sub>7</sub><sup>+</sup>). For C<sub>27</sub>H<sub>38</sub>O<sub>9</sub> (506.6) calculated: 64.02% C, 7.56% H, 0.20% H act.; found: 63.99% C, 7.55% H, 0.22% H act.

*Compound V from lactone IX*: A solution of lactone IX (130 mg) in acetic anhydride (10 ml) was heated in a sealed ampoule to 100°C for 24 h. The mixture was diluted with water, extracted several times with ether and the combined ethereal extracts were worked up as usual. The crude product (96 mg) was purified by thin-layer chromatography affording the enolide V (14 mg). Its identity with a standard was proved by comparison of IR, CD and <sup>1</sup>H NMR spectra.

#### Isolasolide (X)

Repeated chromatography of fraction 7 (Table VII) on a silica gel column gave isolasolide (X; 130 mg), m.p. 120–121°C (light petroleum-ethyl acetate). IR spectrum (cm<sup>-1</sup>): 3 615, 3 525 (hydroxyl), 1 780 (γ-lactone), 1 712 (α,β-unsaturated ester), 1 644 (double bond). Mass spectrum (m/z): 348 (M), 248 (M-100), 230 (M-100-18), 83 (C<sub>4</sub>H<sub>7</sub>CO<sup>+</sup>), 55 (C<sub>4</sub>H<sub>7</sub><sup>+</sup>). For C<sub>20</sub>H<sub>28</sub>O<sub>5</sub> (348.4) calculated: 68.95% C, 8.10% H, 0.29% H act.; found: 68.82% C, 8.08% H, 0.27% H act.

#### Lasolide (III)

Repeated column chromatography of fraction 8 (Table VII) on silica gel afforded lasolide (III; 204 mg), m.p. 166–169°C (light petroleum-ethyl acetate). Its identity with an authentic sample of lasolide<sup>1</sup> was proved by comparison of mass, IR and <sup>1</sup>H NMR spectra and by mixture melting point.

#### 1-(3,4-Methylenedioxy-5-hydroxyphenyl)propan-1-one (XI)

Dry ground roots of *L. trilobum* (8.9 kg) were extracted with light petroleum and then with chloroform. The chloroform extract (142 g) was chromatographed on silica gel (Table VIII). Fraction 5 on crystallization yielded 85 mg of XI, m.p. 159–162°C (ethyl acetate), composition C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>. According to the mass, IR and <sup>1</sup>H NMR spectra and mixture melting point, the compound was identical with an authentic sample<sup>10</sup>.

*Elemental analyses were carried out in the Analytical Laboratory of our Institute by Dr V. Pechanec and Mrs A. Froňková under the direction of Dr J. Horáček. Infrared and CD spectra were taken and interpreted by Dr S. Vašíčková, mass spectra by Dr L. Dolejš. Optical rotations were measured by Mrs Z. Ledvinová. We thank them all.*

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