

## ON TERPENES. CCXIV.\*

THE STRUCTURE OF TWO SESQUITERPENIC LACTONES,  
ISOMONTANOLIDE AND ACETYLISOMONTANOLIDE  
FROM *Laserpitium siler* L.

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From light petroleum extract of the seeds of *Laserpitium siler* L. of Slovenian origin an as yet undescribed sesquiterpenic lactone, isomontanolide (*I*) has been isolated. From light petroleum extract of the roots of the same plant another new sesquiterpenic lactone has been isolated — acetylisomontanolide (*VI*). The structure of both substances was proved by chemical and spectral methods.

In connection with our studies of sesquiterpenic components of *Umbelliferae* we also investigated *Laserpitium siler* L. of Slovenian origin.\*\* From light petroleum extracts of the fruits of this plant we isolated substance *I*, m.p. 176°C,  $[\alpha]_D^{20} -25.2^\circ$ , of the composition  $C_{22}H_{30}O_7$  which according to IR spectra contains a  $\gamma$ -lactone grouping in its molecule (1792 and 1165  $cm^{-1}$ ), an acetyl group (1743 and 1240  $cm^{-1}$ ), an  $\alpha,\beta$ -unsaturated ester group (1704  $cm^{-1}$ , inflexion at 1693  $cm^{-1}$ ), a double bond (1648  $cm^{-1}$ ), and a free hydroxy group (3540  $cm^{-1}$ ). The mass spectrum of the native compound *I* contains a pseudomolecular peak of  $m/e$  306 (406–100) and main fragments of  $m/e$  246 (406–100–60), 228 (406–100–60–18), 83 ( $C_4H_7.CO^+$ ), 55 ( $C_4H_7^+$ ) and the corresponding metastable peak 36.4. The PMR spectrum of the original compound *I* (Table I) indicated the presence of one acetyl group (singlet at 2.03 p.p.m.) and one angeloyl group (quartet of quartets of  $\beta$ -H at 6.18 p.p.m.). Characteristic parameters of the signals of other protons which could be assigned were practically identical with the corresponding parameters of the PMR spectrum of montanolide<sup>1</sup> (*II*). This shows that both substances differ only in the character of the  $\alpha,\beta$ -unsaturated acid group and that the fundamental sesquiterpenic component of both native substances is identical. This conclusion was checked by chemical

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\*\* Fruits and roots of *L. siler* L. were collected in July 1970 near Polhov Gradec, Slovenia, Yugoslavia. For the indication of the locality where the plant grows we are indebted to Prof. T. Wraber, University of Ljubljana.

means: saponification of the native lactone ester *I* gave trihydroxy lactone *III* which according to its IR spectrum and mixture melting point was identical with the substance which we prepared earlier by hydrolysis of montanolide<sup>1</sup> (*II*). From the mentioned facts it follows that the native lactone ester is isomeric with montanolide (*II*), and therefore we propose for it the name isomontanolide. Partial saponification of the native substance *I* gave the non-crystalline monoester *IV* of the composition  $C_{20}H_{28}O_6$ . Its IR spectrum shows the presence of a  $\gamma$ -lactone group ( $1770\text{ cm}^{-1}$ ), an  $\alpha,\beta$ -unsaturated ester ( $1695\text{ cm}^{-1}$ ), a double bond ( $1645\text{ cm}^{-1}$ ), a free hydroxy group ( $3550\text{ cm}^{-1}$ ); no acetyl group was present in the spectrum (absence of absorption at about  $1250\text{ cm}^{-1}$ ) of this substance. The determination of active hydrogen demonstrated two free hydroxy groups in the molecule of deacetylismontanolide *IV*. Its PMR spectrum (Table I) lacks signals of the acetyl group and in its details it corresponds to the PMR spectrum of deacetylmontanolide<sup>1</sup> (*V*). This fact permits the supposition that the acetyl group in the molecule of isomontanolide (*I*) is bound to a tertiary hydroxy group which is located on the carbon in the position 11, similarly as in the molecule of montanolide (*II*). Therefore, we proposed for the molecule of isomontanolide the structure represented by formula I.

From light petroleum extract of the rhizome and the roots of the investigated plant we obtained a native compound *VI*, m.p.  $134^\circ\text{C}$ ,  $[\alpha]_D^{20} -78.2^\circ$ , of the composition  $C_{24}H_{32}O_8$ . Its IR spectra demonstrate the presence of a  $\gamma$ -lactone grouping ( $1783\text{ cm}^{-1}$ ), an acetyl group ( $1733$  and  $1255\text{ cm}^{-1}$ ), an  $\alpha,\beta$ -unsaturated ester (inflexion at  $1705\text{ cm}^{-1}$ ), and a double bond ( $1649\text{ cm}^{-1}$ ). The mass spectrum of compound *VI* contains a pseudomolecular peak of  $m/e$  338 ( $448-60$ ) and main fragments of  $m/e$  288 ( $448-100-60$ ), 83 ( $C_4H_7CO^+$ ), 55 ( $C_4H_7^+$ ), and the corresponding metastable peak 36.4.

Hydrogenation of lactone ester *VI* gave crystalline saturated compound *VII*,  $C_{24}H_{32}O_8$ , the IR spectrum of which proves the presence of a  $\gamma$ -lactone group ( $1785\text{ cm}^{-1}$ ), an acetyl group ( $1730$  and  $1255\text{ cm}^{-1}$ ), and a saturated ester group ( $1730\text{ cm}^{-1}$ ). The spectrum of the saturated lactone ester *VII* contains a pseudomolecular peak  $m/e$  350 ( $542-102$ ) and additional main fragments of  $m/e$  248 ( $452-102-60-42$ ), 230 ( $452-102-60-42-18$ ), 85 ( $C_4H_9CO^+$ ) and 57 ( $C_4H_9^+$ ).

The PMR spectrum of lactone ester *VI* (Table I) contained signals of two acetyl groups (2.11 and 2.01 p.p.m.) and one angeloyl group ( $\beta$ -H 6.08 p.p.m.). Other characteristic parameters (Table I) corresponded to the parameters of the PMR spectrum of isomontanolide (*I*) and montanolide (*II*) (ref.<sup>1</sup>), and indicated that lactone ester *VI* is the acetate of isomontanolide. This supposition was then corroborated directly by acetylation of isomontanolide (*I*) by which we obtained a substance identical with native lactone ester *VI*, as evident from the comparison of their IR and PMR spectra, specific rotation, and mixture melting point. The mentioned facts led us to propose the name acetylismontanolide for the native lactone ester *VI*. Saponification on the native compound *VI* gave a crystalline compound which we pro-

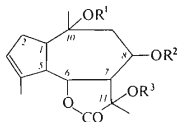
TABLE I  
Characteristic Parameters of the PMR-Spectra

Compound <sup>a</sup>	H <sub>(3)</sub> <sup>c</sup>	H <sub>(6)</sub>	H <sub>(7)</sub>	H <sub>(8)</sub>	H <sub>(13)</sub> <sup>g</sup>	H <sub>(14)</sub> <sup>g</sup>	H <sub>(15)</sub>	Other signals
I	5.55	4.73 $J_{6,7} = 10$ $J_{6,5} = 11$	3.67 $J_{7,6} = 10$ $J_{7,9} = 11$	5.53 <sup>f</sup> $\Sigma J \approx 20$ $J_{8,9} = 1.5$	1.53	1.21	1.88 <sup>h</sup>	CH <sub>3</sub> CO: 2.03 $\beta$ -H <sup>j</sup> : 6.18
IV	5.54	4.59 $J_{6,7} = 10$ $J_{6,5} = 11$	3.11 $J_{7,6} = 10$ $J_{7,8} = 11$	5.61 <sup>f</sup>	1.50	1.22	1.88 <sup>h</sup>	$\beta$ -H <sup>j</sup> : 6.15
VI	5.56	4.74 $J_{6,7} = 10$ $J_{6,5} = 11$	3.67 $J_{7,6} = 10$ $J_{7,8} = 11$	5.67 $J_{8,7} = 11$ $J_{8,9} \approx 11$ $J_{8,9} \approx 2$	1.53	1.59	1.88 <sup>h</sup>	CH <sub>3</sub> CO: 2.01; 2.11 $\beta$ -H <sup>j</sup> : 6.08
VII	—	4.90 $J_{6,7} = 10.5$ $J_{5,6} = 12$	3.55 $J_{7,6} = 10$ $J_{7,8} = 11$	5.48 $J_{8,7} = 11$ $J_{8,9} \approx 11$ $J_{8,9} \approx 2$	1.50	1.50	1.11 <sup>i</sup> $J = 6.5$	$\beta$ -CH <sub>3</sub> <sup>k,i</sup> : 1.13 ( $J = 7$ ) $\beta$ -CH <sub>3</sub> <sup>k</sup> : 0.91 ( $J = 7$ ) CH <sub>3</sub> CO: 2.02; 2.05
III <sup>b</sup>	5.43	4.02 <sup>d</sup> $J_{6,\text{OH}} \approx 5.5$	1.43 <sup>e</sup> $J_{7,8} = 10.5$	4.91 $J_{8,7} = 11$ $J_{8,9} \approx 11$ $J_{8,9} \approx 5.5$	1.20	1.16	1.69	sec. OH: 5.31 tert. OH: 5.35; 5.78 H <sub>(9)</sub> : 2.15 <sup>l</sup> H <sub>(9')</sub> : 1.85 <sup>l</sup>
VIII	5.50	5.22 <sup>d</sup>	1.58 <sup>e</sup> $J_{7,8} = 11$	5.01 $J_{8,7} = 11$ $J_{8,9} = 11$ $J_{8,9} = 5$	1.24	1.20	1.81	CH <sub>3</sub> CO: 2.07

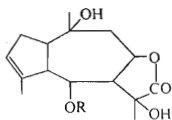
<sup>a</sup> First-order values, solvent deuteriochloroform, internal standard tetramethylsilane, Varian HA-100; <sup>b</sup> solvent hexadeuteriodimethyl sulfoxide; <sup>c</sup> broad unresolved multiplet;  $J_{3,15} \neq 0$  double resonance; <sup>d</sup> broadened singlet;  $J_{5,6}$  and  $J_{6,7}$  were not clearly detectable by double resonance; <sup>e</sup> confirmed by double resonance; <sup>f</sup> overlap with H<sub>(3)</sub> signal; <sup>g</sup> assignment based on the line-width  $W_{1/2}(\text{H}_{(13)}) < W_{1/2}(\text{H}_{(14)})$  or empirical rules (*cf.* text); <sup>h</sup> overlap with angeloyl group methyl signals; approximate position by double resonance;  $J_{3,15} \neq 0$ ; <sup>i</sup> tentative assignment; <sup>j</sup> angelic acid residue; signals of methyl protons overlap with signal of H<sub>(15)</sub>; <sup>k</sup>  $\alpha$ -methylbutyric acid residue; <sup>l</sup>  $J_{9,9'} \approx 13.5$ .

ved to be identical with trihydroxy lactone *III* prepared both from montanolide (*II*) (ref.<sup>1</sup>) and from isomontanolide (*I*). On acetylation of trihydroxy lactone *III* we obtained monoacetate *VIII*,  $C_{17}H_{24}O_6$ , the IR spectrum and active hydrogen determination of which corresponded to our supposition. On the basis of the aforementioned facts we proposed for acetylmontanolide the structure represented by formula *VI*.

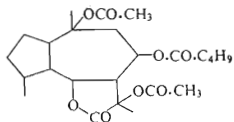
One of the key problems in the solution of the structure of montanolide (*II*), isomontanolide (*I*) and acetylisomontanolide (*VI*) is the position of the  $\gamma$ -lactone ring, and hence, the structure of trihydroxy lactone *III*. This structure could not be proved in the preceding paper on montanolide<sup>1</sup> by PMR spectrum because of the paucity of the available material: it was proposed mainly on the basis of the results of dehydrogenation which afforded linderazulene and artemazulene and on the basis of the PMR spectrum of hydroxyketo lactone *IX* which indicated that the lactone is closed in *IX* at  $C_{(8)}$  and that montanolide (*II*) was relactonised in the course of its saponification, although hydroxyketo lactone *IX* was not derived directly from trihydroxy lactone<sup>1</sup> *III*. Presently we corroborated the structure of *III* by the study of its PMR spectrum in hexadeuteriodimethyl sulfoxide (Table I). As shown by decoupling experiments and exchange reaction with deuterioacetic acid, the spectrum contained a signal for a secondary hydroxy group as a doublet at 5.31 p.p.m. ( $J = 5.5$  Hz). The corresponding methine proton of the  $\underline{CH}-OH$  type formed a doublet at 4.02 p.p.m. ( $J = 5.5$  Hz), and, after exchange, a broadened singlet (in the PMR spectrum of acetate *VIII* as a singlet at 5.52 p.p.m.); hence, it can be assigned to proton  $H_{(6)}$  in agreement with the supposed structure *III* for trihydroxy lactone. Proton  $H_{(8)}$  formed a triplet of doublets at 4.91 p.p.m. ( $J_{8,7} = J_{8,9} = 11$  Hz;  $J_{8,9} = 5.5$  Hz) and an identical multiplet in the PMR spectrum of acetate *VIII* at 5.01 p.p.m. ( $J_{8,7} = J_{8,9} = 11$  Hz;  $J_{8,9} = 5$  Hz). Pronounced differences in the magnitudes of vicinal interactions of proton  $H_{(6)}$  in substances *I*, *II*, *IV*, *V*, and *III* and *VIII*, as well as the direct comparison of the spectra of *VIII* and *IV* indicate clearly the differences in the closure of the  $\gamma$ -lactone ring, as indicated in the proposed structures of these substances: small coupling constants  $J_{5,6}$  and



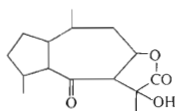
- I*,  $R^1 = H$ ;  $R^2 = CO.C(CH_3)=CH.CH_3$ ;  $R^3 = CO.CH_3$   
*II*,  $R^1 = H$ ;  $R^2 = CO.CH=C(CH_3)_2$ ;  $R^3 = CO.CH_3$   
*IV*,  $R^1, R^3 = H$ ;  $R^2 = CO.C(CH_3)=CH.CH_2$   
*V*,  $R^1, R^3 = H$ ;  $R^2 = CO.CH=C(CH_3)_2$   
*VI*,  $R^1, R^3 = CO.CH_3$ ;  $R^2 = CO.C(CH_3)=CH.CH_3$



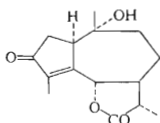
III, R = H  
VIII, R = CO.CH<sub>3</sub>



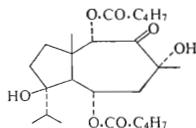
VII



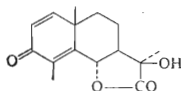
IX



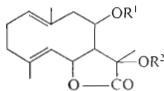
X



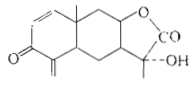
XIV



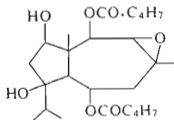
XI



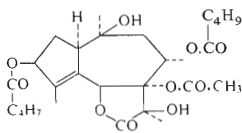
XII, R<sup>1</sup> = CO.C<sub>4</sub>H<sub>7</sub>; R<sup>2</sup> = CO.CH<sub>3</sub>  
XIX, R<sup>1</sup> = R<sup>2</sup> = H



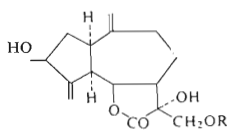
XIII



XV



XVI



XVII, R = H  
XVIII, R = CO.CH<sub>3</sub>

$J_{6,7}$  in compounds III and VIII are not in direct contradiction with their structure and may be explained by different conformation of the unit C<sub>(5)</sub>-C<sub>(6)</sub>-C<sub>(7)</sub> of substances which have the lactone ring closed at C<sub>(6)</sub> and C<sub>(8)</sub>. The small value of the  $J_{6,7}$  interaction for the formally quasi-diaxial configuration of H<sub>(6)</sub> and H<sub>(7)</sub> protons expectable from Dreiding models was already described, for example, in the case of pseudoguaianolides of the helenaline type<sup>2</sup>.

The second key problem is the position of the acetyl group in the molecules of substances I and II. In the preceding paper on montanolide (II) (ref.<sup>1</sup>) it was proposed on the basis of the chemical shifts of protons H<sub>(6)</sub> and H<sub>(8)</sub> in substances II and V.

As a corroboration of the proposal that the acetyl group in the molecules of compounds *I* and *II* is at  $C_{(11)}$ , we may mention directly the chemical shifts of methyl protons  $H_{(13)}$ . As is evident from the comparison of the PMR spectra of isomontanolid (I) and deacetylisomontanolid (IV), as well as of acetylisomontanolid (VI) and tetrahydroacetylisomontanolid VII (Table I) the acetylation of the tertiary hydroxyl strongly affects the position of the signal of one of the tertiary methyl groups, which displayed in the PMR spectrum of compounds *I* and *IV* a shift of approximately 1.20 p.p.m.. Acetylation does not affect the vicinal interaction of protons  $H_{(6)}$ ,  $H_{(7)}$ , and  $H_{(8)}$ , and hence the conformation of the seven-membered ring either. Therefore it can be assumed that the affected tertiary methyl group must be of the  $CH_3-C-OH$  type and that the paramagnetic shift of approximately 0.3 p.p.m. caused by its change to the  $CH_3-C-O.CO.CH_3$  type is rather connected with hyperconjugative effects than with the differences in the anisotropies of the hydroxyl and the acetyl groups. From the comparison of this acetylation shift  $\Delta(CH_3) = \delta(CH_3-C-OAc) - \delta(CH_3-C-OH)$  in other sesquiterpenic hydroxy lactones, containing either the group of the  $CH_3-C_{(10)}-OH$  type (for example derivatives of isophoto- $\alpha$ -santonin lactone (*X*) (refs<sup>3,4</sup>) or  $CH_3-C_{(11)}-OH$  (for example  $\alpha$ -hydroxysantonin (*XI*) (ref.<sup>5</sup>), laserolid (*XII*) (ref.<sup>6</sup>), and farinosin (*XIII*) (refs<sup>7,8</sup>), it followed that this shift is fairly characteristic; usually it applies that  $\Delta(CH_3-C_{(10)}) > \Delta(CH_3-C_{(11)}) > 0$ . The application of this relationship to substances *I* and *IV* leads to the assignment of the acetyl group at  $C_{(11)}$ , as shown in Table I, which is in agreement with the conclusions reported in the preceding paper<sup>1</sup>, as well as with the assignment of the signals of tertiary methyl groups. This assignment also agrees with the supposition that the half-width of the signals of the tertiary methyl group at  $C_{(10)}$  should be larger than in the case of tertiary methyl groups at  $C_{(11)}$  in view of the larger number of possible long-range interactions of the  $CH_3-C-C-H$  type. The steric arrangement of the sesquiterpenic part of isomontanolid (*I*) and acetylisomontanolid (*VI*) is very probably the same as in montanolid (*II*) (ref.<sup>1</sup>), and it will be the object of a further communication.

The structures of both native substances, isomontanolid (*I*) and acetylisomontanolid (*VI*), represent good evidence that sesquiterpenic oxygenated substances, and especially sesquiterpenic lactones present in some species of *Laserpitineae* tribe (*Umbelliferae* family), contain the basic sesquiterpenic skeleton of the molecule relatively richly substituted by oxygen-containing functions, as for example laserpitin (*XIV*) (ref.<sup>9</sup>), isolaserpitin (*XV*) (ref.<sup>10</sup>), and other compounds from *L. latifolium* L., laserolid (*XII*) (ref.<sup>6</sup>) and trilobolid (*XVI*) (ref.<sup>11</sup>) from *L. trilobum* (L.) BORKH., and further montanolid (*II*) and silerolid from *L. siler* L. of Bulgarian origin<sup>1</sup>. For sesquiterpenic lactones of the species of this tribe the substitution at  $C_{(11)}$  with a tertiary hydroxy group, usually esterified with acetic acid, seems typical, as is evident from the case of laserolid (*XII*) (ref.<sup>6</sup>), trilobolid (*XVI*) (ref.<sup>11</sup>), montanolid (*II*) (ref.<sup>1</sup>), and isomontanolid (*I*) and acetylisomontanolid (*VI*), the native

lactones described in this paper. The substitution by oxygen-containing groups at  $C_{(11)}$  is quite exceptional among more than 400 sesquiterpenic lactones isolated from various species of *Compositae*; this is shown by the fact that the mentioned substitution at  $C_{(11)}$  was described only in farinosin (*XIII*) refs<sup>7,8</sup>), solstitialin (*XVII*) (ref.<sup>12</sup>), solstitialin acetate (*XVIII*) (ref.<sup>13</sup>) and hydroxybalchanolide (*XIX*) (ref.<sup>14</sup>). According to newer views the structure of hydroxybalchanolide and especially the location of the tertiary hydroxy group at  $C_{(11)}$  cannot be considered as proved. Finally, it should be mentioned that we were able to isolate montanolide (*II*) from the roots of *L. siler* L. of Bulgarian origin while now – from a plant from Slovenia – we have isolated acetylismontanolide (*IV*). These substances, although their basic sesquiterpenic parts are absolutely identical, are not identical, and the difference in structure consists in the esterification of the hydroxy groups of the sesquiterpenic parts of their molecules by different acids. Although similar modification of the structure of the components, depending on the locality where the plant was grown is known<sup>15</sup>, we consider that a botanical comparison of the representatives of the investigated plant from both localities will be necessary, especially in view of the occurrence of a subspecies of *L. siler* L. on the Balkan peninsula<sup>16,17</sup>.

## EXPERIMENTAL

The melting points were determined on a Kofler block and they were not corrected. For column chromatography silica gel according to Pitra and Štěrbá<sup>18</sup> was used (30–60  $\mu$ , deactivated by the addition of 11% of water), while for thin layer chromatography silica gel Merck according to Stahl was employed. The infrared spectra were measured in chloroform on Unicam S.P. 200 and Zeiss UR-10 (Jena). The PMR spectra were measured in deuteriochloroform unless stated otherwise, on a Varian HA-100 apparatus (tetramethylsilane as internal standard). Mass spectra were measured on an AEI MS 902 spectrograph. Optical rotation was determined on Jasco UV-5 spectropolarimeter in methanol, unless stated otherwise.

### Isomontanolide (I)

Ground fruits (5.5 kg) of *L. siler* L. of Slovenian origin were gradually extracted with light petroleum (b.p. 40–60°C) and single fractions were evaporated. The viscous residue (910 g) had the characteristic odour of these fruits. From the last extracts isomontanolide (*I*; 1.6 g) crystallised out, m.p. 174–176°C (diisopropyl ether),  $[\alpha]_D^{20}$  –25.2° (c 0.18; chloroform),  $R_F$  0.75 (benzene-ether 2:1). For  $C_{22}H_{30}O_7$  (406.5) calculated: 65.00% C, 7.26% H, 0.25% H act.; found: 65.27% C, 7.49% H, 0.29% H act.

### Trihydroxy Lactone III

Isomontanolide (*I*; 180 mg) was dissolved in 10 ml of 5% methanolic potassium hydroxide and the solution was allowed to stand at room temperature for 18 hours. The mixture was diluted with water, acidified, and extracted with chloroform. The combined chloroform extracts were washed with a sodium hydrogen carbonate solution, dried, and evaporated to dryness. The residue, trihydroxy lactone *III*, was crystallised from diisopropyl ether and methanol, m.p. 192 to 193°C. The mixture melting point with trihydroxy lactone *III* prepared from montanolide (*II*) (m.p. 194°C) was undepressed. The IR spectra of trihydroxy lactone, *III* both prepared from montanolide (*II*) (ref.<sup>1</sup>) and from isomontanolide (*I*), were identical.

Deacetylisomontanolide (*IV*)

Isomontanolide (*I*; 500 mg) dissolved in 30 ml of methanol was mixed with a solution of 438 mg of potassium carbonate in 8 ml of water and the mixture was allowed to stand at room temperature for 2.5 hours. Methanol was distilled off under reduced pressure and the residue diluted with water and extracted with chloroform. The residue (300 mg) was chromatographed on 30 g of silica gel with benzene, containing 2% of ether. From the latter fractions monoester *IV* was obtained in the form of a viscous liquid of  $R_F$  0.67 (benzene-ether 1 : 1). For  $C_{20}H_{28}O_6$  (364.4) calculated: 65.91% C, 7.74% H, 0.55% H act. (2); found: 65.70% C, 7.87% H, 0.56% H act.

Acetylisomontanolide (*VI*)

Ground, dried rhizomes and roots (14.9 kg) of *L. siler* L. of Slovenian origin were extracted with light petroleum. From the residue acetyl isomontanolide (*VI*) crystallised out, m.p. 134°C (diisopropyl ether)  $[\alpha]_D^{20}$  -78.2° (c 0.14). For  $C_{24}H_{32}O_8$  (448.5) calculated: 64.27% C, 7.19% H; found: 64.48% C, 7.02% H.

Tetrahydroacetylisomontanolide (*VII*)

A solution of acetyl isomontanolide (*VI*; 219 mg) in 10 ml of acetic acid was added with 35.5 mg of  $PtO_2$  (Adams catalyst) and then saturated with hydrogen. The consumption, 33 ml (25°C, 734 Torr), corresponds to the saturation of 2.1 double bonds. The conventional work-up gave tetrahydro derivative *VII* (210 mg), m.p. 153°C (diisopropyl ether) and  $[\alpha]_D^{20}$  -67.5° (c 0.107). For  $C_{24}H_{36}O_8$  (452.5) calculated: 63.70% C, 8.02% H; found: 63.62% C, 8.17% H.

Trihydroxy Lactone *III*

Acetyl isomontanolide (*VI*; 2.0 g) was dissolved in a solution of 5 g potassium hydroxide in 100 ml of water and the mixture was allowed to stand at room temperature for 20 hours. The solvent was distilled off under reduced pressure almost to dryness and the residue was diluted with water, then acidified with 5% sulfuric acid, and extracted with chloroform. The combined chloroform fractions were worked up in the conventional manner and trihydroxy lactone *III* was obtained, m.p. 194–195°C (diisopropyl ether, methanol) and  $[\alpha]_D^{20}$  -38.2° (c 0.48). Mixture melting point with trihydroxy lactone *III* obtained from montanolide (*II*) (ref.<sup>1</sup>) on one hand and from isomontanolide (*I*) on the other was undepressed. The IR spectra of trihydroxy lactone *III* obtained from *II*, *I* and also *VI* were identical. Acetate *VIII*: A mixture of trihydroxy lactone *III* (568 mg), 0.25 ml of acetic anhydride, and 1.5 ml of pyridine was allowed to stand at room temperature for 20 hours. Acetate *VIII* was prepared in the usual manner (430 mg), m.p. 205°C (diisopropyl ether),  $[\alpha]_D^{20}$  -27.8° (c 0.22). For  $C_{17}H_{24}O_6$  (324.4) calculated: 62.96% C, 7.46% H, 0.62% act.; found: 63.21% C, 7.53% H, 0.78% H act.

Acetylisomontanolide (*VI*) from Isomontanolide (*I*)

A solution of isomontanolide (*I*; 100 mg) in 8 ml of acetic anhydride was heated in a sealed ampoule at 100°C (bath temperature) for 24 hours. The mixture was diluted with water, extracted with ether, and the combined ethereal extracts were worked up in the conventional manner. A viscous liquid (86 mg) was obtained which was chromatographed on 4 g of silica gel with benzene containing 2% of ether. From the first fractions acetyl isomontanolide (*VI*) was isolated, m.p. 135°C (diisopropyl ether),  $[\alpha]_D^{20}$  -70.4° (c 0.046; chloroform). The mixture melting point



with native acetyl isomontanolid (m.p. 134°C) was undepressed. The IR and PMR spectra of both substance were identical.

*The elemental analyses were carried out in the Analytical Department of our Institute (head Dr J. Horáček) by Mrs V. Rusová, Mr V. Štěřba, and Mrs L. Pejchalová. The IR spectra were measured by Mrs S. Holubová and Mrs K. Matoušková. Optical rotation was measured by Mrs H. Pilařová. The mass spectra were recorded by Mrs M. Vokáčová and Mrs M. Kabelíková under the direction of Dr L. Dolejš. We are grateful to all those mentioned for their contributions as well as to Mrs M. Snopková, Miss H. Němcová, and Miss P. Jeklová for their technical assistance.*

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