

## ON TERPENES. CCXXII.\*

THE STRUCTURE OF ARCHANGELOLIDE, A SESQUITERPENIC LACTONE FROM *Laserpitium archangelica* WULF.

M.HOLUB and Z.SAMEK

*Institute of Organic Chemistry and Biochemistry,  
Czechoslovak Academy of Sciences, Prague 6*

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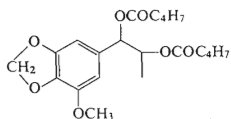
From the roots of *Laserpitium archangelica* WULF.  $\beta$ -sitosterol, laserin (*II*), 3,4-methylenedioxy-5-methoxypropiofenone (*III*), and a new sesquiterpenic lactone — archangelolide — were isolated. The latter was also isolated from the fruits of the same species. On the basis of the PMR spectra of the native substance and their derivatives, as well as on the basis of chemical correlation with acetylismontanolide (*IV*), structure *I* was inferred for archangelolide.

From the roots of several species of *Laserpitium* a series of sesquiterpenic substances has been isolated<sup>1-11</sup>. In this paper we describe substances from the roots and the rhizomes of *L. archangelica* WULF. (*Umbelliferae*.) From the dry residue of the light petroleum extract substance *I* crystallised out, the IR and PMR spectra of which indicated that it is an as yet undescribed sesquiterpenic  $\gamma$ -lactone to which we gave the name archangelolide. On chromatography of the crude extract we also isolated in addition to archangelolide (*I*) the already described laserin<sup>4</sup> (*II*), 3,4-methylenedioxy-5-methoxypropiofenone<sup>2,12-15</sup> (*III*),\*\* and  $\beta$ -sitosterol, which were identified by comparison with authentic samples.

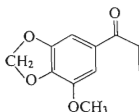
Archangelolide (*I*), of m.p. 69–71°C and  $[\alpha]_D + 35.8^\circ$ , displayed in its IR spectrum absorption bands of a  $\gamma$ -lactone group (1791 and 1150  $\text{cm}^{-1}$ ), a saturated ester group (1738  $\text{cm}^{-1}$ ), and  $\alpha,\beta$ -unsaturated ester group (1713  $\text{cm}^{-1}$ ), a double bond (1651  $\text{cm}^{-1}$ ), and an acetate group (1240  $\text{cm}^{-1}$ ). Its PMR spectrum (Table I) indicated the presence of an O-angelyl group, an O- $\alpha$ -methylbutyryl group, and two acetyl groups. Its mass spectrum indicated the presence of a fragment of maximum mass  $m/e$  488, further fragments of  $m/e$  388 (488–100), 326 (488–102–60), 286 (488–100–102), and 226 (488–100–102–60). In accordance with the PMR and IR spectra the mass spectrum of archangelolide contained peaks of fragments of  $m/e$  43 ( $\text{CH}_3\text{CO}^+$ ), 55 ( $\text{C}_4\text{H}_7^+$ ), 57 ( $\text{C}_4\text{H}_9^+$ ), 83 ( $\text{C}_4\text{H}_7\text{CO}^+$ ), 85 ( $\text{C}_4\text{H}_9\text{CO}^+$ ) and 100 ( $\text{C}_4\text{H}_7\text{COOH}$ ).

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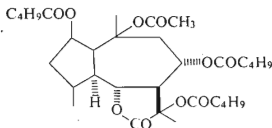
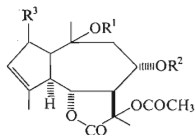
\*\* For this compound we use chemical nomenclature and consider both trivial names, crocatone<sup>14,15</sup> and latifolone<sup>4,9</sup> as superfluous.



II



III



V

I,  $R^1 = \text{COCH}_3$ ;  $R^2 = \text{COCH}(\text{CH}_3)\text{C}_2\text{H}_5$ ;  $R^3 = \text{OCOC}(\text{CH}_3) = \text{CHCH}_3$

IV,  $R^1 = \text{COCH}_3$ ;  $R^2 = \text{COC}(\text{CH}_3) = \text{CHCH}_3$ ;  $R^3 = \text{H}$

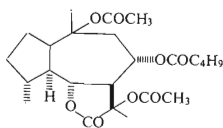
VI,  $R^1 = \text{H}$ ;  $R^2 = \text{COCH} = \text{C}(\text{CH}_3)_2$ ;  $R^3 = \text{H}$

VII,  $R^1 = \text{H}$ ;  $R^2 = \text{COC}(\text{CH}_3) = \text{CHCH}_3$ ;  $R^3 = \text{H}$

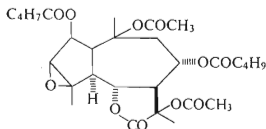
XI,  $R^1 = \text{COCH}_3$ ;  $R^2 = \text{COCH}(\text{CH}_3)\text{C}_2\text{H}_5$ ;  $R^3 = \text{OCOC}_4\text{H}_7\text{O}$

In view of the presence of the fragments of  $m/e$  226 and 326, indicating the elimination of a single molecule of acetic acid, it was possible to assume that the second O-acetyl group, which was demonstrated by the PMR spectrum, could be easily eliminated, and that the fragment of  $m/e$  488 is pseudomolecular  $M' = M - 60$ , similarly as in acetylisomontanolid<sup>10</sup> (IV), for example. The mass  $M = 548$  corresponds to the elemental composition  $\text{C}_{29}\text{H}_{40}\text{O}_{10}$  for archangelolide (I). By hydrogenation of archangelolide (I) on  $\text{PtO}_2$  in acetic acid we obtained compound V which according to its elemental analysis, PMR, IR and mass spectrum was a saturated tetraester of the composition  $\text{C}_{29}\text{H}_{44}\text{O}_{10}$ , containing two O-acetyl groups and two  $\alpha$ -methylbutyryl groups in the molecule. From these facts it followed that the molecule of archangelolide (I) contained two acetate groups, one residue of angelic acid, one of  $\alpha$ -methylbutyric acid, and a basic fifteen-carbon bicyclic skeleton with one double bond and a  $\gamma$ -lactone ring. The character of the skeleton was deduced directly from a detailed analysis of the PMR spectrum of archangelolide (I) by multiple resonance experiments (Table I). From the observed distribution of the chemical shifts and the topological continuity of vicinal and long-range couplings (Table I) of protons it followed that its skeleton is a 3-guaiane with three esterified secondary hydroxyls, on  $\text{C}_{(2)}$ ,  $\text{C}_{(6)}$ , and  $\text{C}_{(8)}$ , and with two esterified tertiary hydroxyls, on  $\text{C}_{(10)}$  and  $\text{C}_{(11)}$ . The observed values of vicinal couplings of protons on the fragment  $\text{C}_{(5)}$  to  $\text{C}_{(9)}$  (Table I) indicated the same relative configuration (*i.e.*  $5\alpha\text{-H}$ ,  $6\beta\text{-H}$ ,  $7\alpha\text{-H}$ ,  $8\beta\text{-H}$ ) and hence also the same conformation

of the seven-membered rings as in montanolide<sup>9</sup> (VI), isomontanolide<sup>10</sup> (VII), and acetylisomontanolide<sup>10</sup> (IV); hence, the orientation of the  $\gamma$ -lactone ring at C<sub>(6)</sub> is also the same.



IX



X

These conclusions were confirmed by direct chemical correlation of archangelolide (I) with acetylisomontanolide<sup>10</sup> (IV). Hydrogenation of archangelolide (I) in acetic acid on 30% palladized charcoal gave tetrahydroarchangelolide (V) and two triester lactones, VIII and IX, of the same composition C<sub>24</sub>H<sub>34</sub>O<sub>8</sub>, which according to their PMR spectra (Table I) contained two O-acetyl groups and one  $\alpha$ -methylbutyryl group, bound to C<sub>(10)</sub>, C<sub>(11)</sub>, and C<sub>(8)</sub>. The saturated triester lactone IX was identical according to its IR, PMR, and mass spectrum with the tetrahydroacetylisomontanolide<sup>10</sup> (IX) described earlier. Triester lactones VIII and IX differed only by the configuration of the methyl group at C<sub>(4)</sub>. Relative configurations of this group were assigned on the basis of the determined magnitudes of average vicinal coupling of methyl protons  $H_{(15)}$  ( $J_{4,15} = 7.2$  (VIII) and  $J_{4,15} = 6.8$  (IX)), from which the 4 $\beta$  configuration of the methyl in triester VIII and the 4 $\alpha$  configuration of this group in compound IX follows on the basis of the rule for  $^3J_{\text{CH}_3-\text{CH}}$  on the CH<sub>3</sub>—CH—CH' fragment  $^3J_{\text{CH}_3}(\text{H}, \text{H}' \text{ anti-periplanar}) > ^3J_{\text{CH}_3}(\text{H}, \text{H}' \text{ syn-periplanar})$ , under the supposition of  $\alpha$ -configuration of the proton H<sub>(5)</sub> (ref.<sup>16,17</sup>). From the formation of tetrahydroacetylisomontanolide<sup>10</sup> (IX) from archangelolide (I) an unambiguous localisation of the acetyl groups in its molecule followed, i.e. on C<sub>(10)</sub> and C<sub>(11)</sub>, as well as the localisation of one bound C<sub>5</sub>-acid residue esterifying the hydroxyl at C<sub>(8)</sub>. The decision, which of the two C<sub>5</sub>-acid residues is bound to C<sub>(2)</sub> and which to C<sub>(8)</sub>, was carried out in the following manner: On oxidation of archangelolide (I) with *m*-chloroperbenzoic acid we obtained a mixture of compounds from which we isolated a small amount of epoxide X and a fraction XI containing according to its PMR and mass spectrum a mixture of substances with the retained  $\Delta^3$  double bond and variously oxidized angelic acid residue. We hydrogenated this fraction XI without further separation under conditions suitable for hydrogenolysis, as mentioned in the section on hydrogenolysis of archangelolide (I).

From the mixture of hydrogenation products we isolated a product, C<sub>24</sub>H<sub>34</sub>O<sub>8</sub>, which according to its PMR spectrum was a mixture of triester lactones VIII and IX.

TABLE I  
Characteristic Parameters of the PMR Spectra of Archangelolide and Its Derivatives

Compound <sup>a</sup>	H <sub>1</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>
<i>I</i> <sup>b</sup>	3.32 <i>J</i> <sub>1,2</sub> 3.5 <i>J</i> <sub>1,5</sub> 8.0	—	3.03 <sup>c</sup>	4.80 <i>J</i> <sub>6,5</sub> 11.5 <i>J</i> <sub>6,7</sub> 9.7	3.62 <i>J</i> <sub>7,6</sub> 9.7 <i>J</i> <sub>7,8</sub> 11.4
<i>V</i> <sup>e</sup>	3.13 <i>J</i> <sub>1,2</sub> 7.5 <i>J</i> <sub>1,5</sub> 7.5	2.30 <sup>d</sup>	2.10 <sup>d</sup>	4.62 <i>J</i> <sub>6,5</sub> 11.5 <i>J</i> <sub>6,7</sub> 10.0	3.61 <i>J</i> <sub>7,6</sub> 10 <i>J</i> <sub>7,8</sub> 10.5
<i>VIII</i> <sup>f</sup>	—	2.60 <sup>d</sup>	1.85 <sup>d</sup>	4.60 <i>J</i> <sub>6,5</sub> 12.1 <i>J</i> <sub>6,7</sub> 10.2	3.60 <i>J</i> <sub>7,6</sub> 10.2 <i>J</i> <sub>7,8</sub> 11.2
<i>IX</i> <sup>h</sup>	—	2.30 <sup>d</sup>	2.25 <sup>d</sup>	4.90 <i>J</i> <sub>6,7</sub> 10.0 <i>J</i> <sub>6,5</sub> 12.0	3.55 <i>J</i> <sub>7,6</sub> 10.0 <i>J</i> <sub>7,8</sub> 11.2
<i>X</i> <sup>i</sup>	3.00 <i>J</i> <sub>1,2</sub> 7.9 <i>J</i> <sub>1,5</sub> 7.1	—	2.64 <i>J</i> <sub>5,6</sub> 12.2 <i>J</i> <sub>5,1</sub> 7.1	4.76 <i>J</i> <sub>6,5</sub> 12.2 <i>J</i> <sub>6,7</sub> 9.8	3.65 <i>J</i> <sub>7,6</sub> 9.9 <i>J</i> <sub>7,8</sub> 10.9

From the course of the mentioned hydrogenolysis it followed unambiguously that the residue of angelic acid is at C<sub>(2)</sub>, and that of  $\alpha$ -methylbutyric acid, at C<sub>(8)</sub>. The sum of the mentioned facts shows that the structure with a partial relative stereostructure represented by formula *I* should be assigned to archangelolide. The sterical arrangement on the chirality centers at C<sub>(1)</sub>, C<sub>(5)</sub>, C<sub>(6)</sub>, C<sub>(7)</sub>, C<sub>(8)</sub>, C<sub>(10)</sub>, and C<sub>(11)</sub> in archangelolide (*I*) is the same as in montanolide<sup>9</sup> (*VI*), isomontanolide<sup>10</sup> (*VII*), and acetylismontanolide<sup>10</sup> (*IV*).

The structure of archangelolide (*I*) represents a further example of a relatively rich substitution by oxygen-containing functions of the basic skeleton of sesquiterpenic lactones present in the species of *Laserpitineae* tribe (*Umbelliferae*); this was stated already in a preceding paper<sup>10</sup>. Moreover, archangelolide (*I*) is the first and only tetraester described in the field of sesquiterpenic lactones so far. In analogy to the majority of sesquiterpenic lactones which were already isolated from the species

TABLE I  
(Continued)

H <sub>8</sub>	H <sub>9</sub>	H <sub>9'</sub>	H <sub>13</sub>	H <sub>14</sub>	H <sub>15</sub>
5.61 <i>J</i> <sub>8,9</sub> 2.7 <i>J</i> <sub>8,9'</sub> 11.0 <i>J</i> <sub>8,7</sub> 11.0	2.60 <i>J</i> <sub>9,8</sub> 2.7 <i>J</i> <sub>9,9'</sub> 15	2.04 <sup>d</sup>	1.56	1.42	1.93 <i>J</i> <sub>15,3</sub> ≠ 0 <i>J</i> <sub>15,5</sub> ≠ 0 <i>J</i> <sub>15,2</sub> ≠ 0
5.55 <i>J</i> <sub>8,9</sub> < 2 <i>J</i> <sub>8,9'</sub> 10.5 <i>J</i> <sub>8,7</sub> 10.5	2.52 <i>J</i> <sub>9,9'</sub> 15	1.92 <sup>d</sup> <i>J</i> <sub>9',8</sub> 10.5	1.52	1.52	1.10 <i>J</i> <sub>15,4</sub> 7.0
5.53 <i>J</i> <sub>8,9</sub> ≅ 1 <i>J</i> <sub>8,9'</sub> 10 <i>J</i> <sub>8,7</sub> 11	2.48 9,9', 15	1.85 <i>J</i> <sub>9',9</sub> 15 <i>J</i> <sub>9',8</sub> 10	1.51 <sup>g</sup>	1.53 <sup>g</sup>	0.99 <i>J</i> <sub>15,4</sub> 7.2
5.47 <i>J</i> <sub>8,9</sub> 2.5 <i>J</i> <sub>8,9'</sub> 10.9 <i>J</i> <sub>8,7</sub> 10.9	2.49 <i>J</i> <sub>9,9'</sub> 15	1.96 <i>J</i> <sub>9',9</sub> 15 <i>J</i> <sub>9',8</sub> 10.5	1.51	1.51	1.12 <i>J</i> <sub>15,4</sub> 6.8
5.44 <i>J</i> <sub>8,9</sub> 2.6 <i>J</i> <sub>8,9'</sub> 10.6 <i>J</i> <sub>8,7</sub> 10.6	2.57 <i>J</i> <sub>9,8</sub> 2.5 <i>J</i> <sub>9,9'</sub> 15	2.02 <sup>d</sup>	1.54 <sup>g</sup>	1.54 <sup>g</sup>	1.63 <sup>g</sup>

<sup>a</sup>All spectra were measured on a Varian HA-100 instrument using deuteriochloroform as a solvent and tetramethylsilane as an internal reference. Chemical shifts are given in  $\delta$ (TMS)-scale and splittings in Hz (first-order analysis). The assignments of signals were confirmed by decoupling experiments. <sup>b</sup>O-Angelyl —  $\beta$ -H: 6.04 qq; O- $\alpha$ -methylbutyryl —  $\alpha$ -H: 2.29 m ( $J \approx 7$ ),  $\alpha$ -CH<sub>3</sub>: 1.14 d ( $J \approx 7$ ) and  $\beta$ -CH<sub>3</sub>: 0.92 t ( $J \approx 7$ ); O-acetyls — 2.00 and 2.06 (s); H<sub>2</sub> 5.82; H<sub>3</sub> 5.65; <sup>c</sup>Broad doublet of doublets, <sup>3</sup> $J \approx 20$  Hz. <sup>d</sup>Approximate position from DR-experiments. <sup>e</sup>Spectrum obscured, due to impurities; O- $\alpha$ -methylbutyryl —  $\alpha$ -H and  $\alpha$ -H': 2.30 (DR),  $\alpha$ -CH<sub>3</sub>: 1.12 d ( $J \approx 7$ ),  $\alpha$ -CH<sub>3</sub>': 1.11 d ( $J \approx 7$ ),  $\beta$ -CH<sub>3</sub>: 0.92 t ( $J \approx 7$ ) and  $\beta$ -CH<sub>3</sub>': 0.89 t ( $J \approx 7$ ); O-acetyls — 2.04 (s, 6H); H<sub>2</sub> 5.10. <sup>f</sup>O- $\alpha$ -Methylbutyryl:  $\alpha$ -CH<sub>3</sub>: 1.14 d ( $J \approx 7$ ) and  $\beta$ -CH<sub>3</sub>: 0.93 t ( $J \approx 7$ ); O-acetyls: 2.04 and 2.10 (s). <sup>g</sup>Tentative assignment. <sup>h</sup>O- $\alpha$ -Methylbutyryl:  $\alpha$ -CH<sub>3</sub>: 1.14 d ( $J \approx 7$ ) and  $\beta$ -CH<sub>3</sub>: 0.92 t ( $J \approx 7$ ); O-acetyls: 2.02 and 2.05 (s). <sup>i</sup>O- $\alpha$ -Methylbutyryl:  $\alpha$ -CH<sub>3</sub>: 1.14 d ( $J \approx 7$ ) and  $\beta$ -CH<sub>3</sub>: 0.92 t ( $J \approx 7$ ); O-acetyls: 2.06 and 1.99 (s); O-angelyl:  $\beta$ -H: 6.08 qq; H<sub>2</sub> 5.29,  $J_{2,1} = 8.0$ ,  $J_{2,3} = 1.8$ ; H<sub>3</sub> = 3.56,  $J_{3,2} = 1.7$ .

of the mentioned tribe, in archangelolide too the oxygen-containing substituent is at  $C_{(11)}$ . The structure of archangelolide (*I*) is also interesting because its basic sesquiterpenic moiety has the same structure, including the configuration and conformation, as montanolide<sup>9</sup> (*VI*), isomontanolide<sup>10</sup> (*VII*), and acetylisomontanolide<sup>10</sup> (*IV*), but its angelic acid residue is bound to the hydroxyl at  $C_{(2)}$  and not at  $C_{(8)}$  as is the case in compounds *VI*, *VII* and *IV*. Considering the localisation of the  $\alpha$ -methylbutyryl residue in the position  $C_{(8)}$  and the angelyl residue in the  $\alpha$ -position to the skeletal double bond, and disregarding other similarities and differences, archangelolide shows a certain structural analogy with trilobolide<sup>6,7</sup> (*XII*) which we isolated from *Laser trilobum* (L.) BORKH., closely related to the species of *Laserpitium*. The presence of lactone *I* in *L. archangelica* is additional evidence of a certain relationship between *Umbelliferae* and *Compositae*, because the sesquiterpenic lactones are a typical component of the species of *Compositae*.

## EXPERIMENTAL

Melting points were determined on a Kofler block and they were not corrected. For column chromatography silica gel according to Pitra and Štěrba<sup>18</sup> (30–60  $\mu$ , deactivated by addition of 11% of water) was used. For thin layer chromatography silica gel G Merck was used. IR spectra were measured in chloroform on a Unicam SP 200 spectrophotometer. PMR spectra were measured in deuteriochloroform, unless stated otherwise, on a Varian HA-100 apparatus. Mass spectra were measured on an AEI MS 902 spectrograph. Optical rotation was determined with an objective polarimeter in methanol.

### Isolation of Substances

A) *Roots*: Dry, ground roots (2.4 kg) of *Laserpitium archangelica* WULF., collected in June 1965 on the southern and south-eastern slopes close to the top of Revaň mountain (Martinské hole, Slovakia), were extracted with light petroleum. From the residue archangelolide (*I*) crystallised out, m.p. 69–71°C (ether),  $[\alpha]_D^{20} +35.8^\circ$ . For  $C_{29}H_{40}O_{10}$  (548.6) calculated: 63.49% C, 7.35% H; found: 63.70% C, 7.62% H. The residue (35 g) was chromatographed on silica gel (350 g) with benzene, giving a mixture of laserin<sup>4</sup> (*II*) and 3,4-methylenedioxy-5-methoxypropiofenone<sup>2</sup> (*III*). After distillation of the mixture *in vacuo* (approx. 1 Torr) substance *III* crystallised out, m.p. 88–89°C (light petroleum), which melted undepressed on admixture of an authentic sample and also had identical infrared spectrum. The liquid fraction after the separation of *III* was purified by column chromatography on silica gel, giving liquid laserin<sup>4</sup> (*II*) identical according to its IR spectrum with an authentic specimen. From a later fraction  $\beta$ -sitosterol was isolated, m.p. 137°C (methanol), which was identified on the basis of its spectrum and mixture melting point with a standard.

B) *Fruits*: Dry, ground fruits (1.3 kg), collected in July 1971 in the same locality as above were extracted with light petroleum and concentrated. From the residue archangelolide (*I*) crystallised out, m.p. 69–71°C (ether), identical according to its IR spectrum and mixture melting point with the substance isolated under A).

### Tetrahydroarchangelolide (*V*)

A mixture of archangelolide (*I*; 1.42 g), 50 ml acetic acid, and 131 mg of  $PtO_2$  was saturated with hydrogen; consumption was 182 ml of hydrogen (25°C, 738 Torr). Conventional work-up gave tetrahydroarchangelolide (*V*; 1.29 g), m.p. 136–137°C (diisopropyl ether),  $[\alpha]_D -54.3^\circ$  (*c* 0.14).

$R_F$  0.35 (light petroleum-acetone-moist ether 5 : 1 : 1). For  $C_{29}H_{44}O_{10}$  (552.6) calculated: 63.08% C, 8.02% H; found: 63.23% C, 8.09% H. IR spectrum: 2950, 1780 ( $\gamma$ -lactone), 1725 (saturated ester), 1465, 1370, 1245 (acetate), 1145, 1100, 1075, 1020  $cm^{-1}$ . Mass spectrum:  $m/e$  492 (552 - 60), 450 (552 - 102), 390 (552 - 102 - 60), 330 (552 - 102 - 60 - 60), 228 (552 - 102 - 60 - 60 - 102), 85 ( $C_4H_9CO^+$ ), 57 ( $C_4H_9^+$ ) (metastable 38.2), and 60 ( $CH_3COOH$ ).

#### Hydrogenolysis of Archangelolide

A mixture of archangelolide (*I*; 532 mg), 20 ml of acetic acid, 121 mg of 30% Pd/C catalyst, and a few crystals of *p*-toluenesulfonic acid was saturated with hydrogen for 4 days. After conventional working up a product (450 mg) was obtained which according to thin-layer chromatography contained at least two substances. It was chromatographed on a silica gel column (50 g), using benzene with 5% ether as eluent. Triester *VIII* was eluted first, m.p. 118–120°C (diisopropyl ether),  $R_F$  0.4 (light petroleum-acetone-moist ether 5 : 2 : 2). Mass spectrum:  $m/e$  392 (452 - 60), 350 (452 - 102), 290 (452 - 102 - 60), 230 (452 - 102 - 60 - 60), 85 ( $C_4H_9CO^+$ ), 57 ( $C_4H_9^+$ ) (metastable 38.2), and 60 ( $CH_3COOH$ ). IR spectrum: 2920, 1774 ( $\gamma$ -lactone), 1725 (saturated ester), 1465, 1380, 1245 (acetate), 1145, 1095, 1080, 1020  $cm^{-1}$ . Almost simultaneously with the triester *VIII* the saturated triester *IX* was also eluted, m.p. 129–131°C (diisopropyl ether),  $[\alpha]_D -41.8^\circ$  (*c* 0.25).  $R_F$  0.4 (light petroleum-acetone-moist, ether 5 : 2 : 2). Mass spectrum:  $m/e$  350 (452 - 102), 332 (452 - 60 - 60), 290 (452 - 102 - 60). 230 (452 - 102 - 60 - 60), 85 ( $C_4H_9CO^+$ ), 57 ( $C_4H_9^+$ ) (metastable 38.2) and 60 ( $CH_3COOH$ ), IR spectrum: 2950, 1775 ( $\gamma$ -lactone), 1725 (saturated ester), 1470, 1370, 1250 (acetate), 1145, 1105, 1075, 1020  $cm^{-1}$ . Mixture melting point of this compound (*IX*) with an authentic specimen of tetrahydroacetylismontanolid<sup>10</sup> (*IX*) was undepressed. In further fractions tetrahydroarchangelolide (*V*) of m.p. 145°C (diisopropyl ether), came out  $[\alpha]_D -56.6^\circ$  (*c* 0.5), and  $R_F$  0.35 (light petroleum-acetone-moist ether 5 : 2 : 2), identical according to its IR spectrum and mixture melting point with the substance obtained in the preceding experiment.

#### Epoxidation of Archangelolide (*I*)

A mixture of archangelolide (*I*; 1.0 g), 250 ml of chloroform, and 335 mg of 85% *m*-chlorobenzoic acid was refluxed for 90 minutes. The solvent was distilled off and the product (1.0 g) chromatographed on a column of 100 g of silica gel using benzene with 5% of ether as eluent. First fractions contained in addition to the starting compound also traces of epoxide *X*. Medium fractions afforded the product *XI* (480 mg), m.p. 60–63°C,  $[\alpha]_D -69.7^\circ$  (*c* 0.42).  $R_F$  0.35 (benzene-ether 4 : 1). For  $C_{29}H_{40}O_{11}$  (564.6) calculated: 61.68% C, 7.14% H; found: 61.30% C, 7.37% H. Mass spectrum:  $m/e$  448 (564 - 116), 388 (564 - 116 - 60), 286 (564 - 116 - 60 - 102), 226 (564 - 116 - 60 - 102 - 60), 85 ( $C_4H_9CO^+$ ), 57 ( $C_4H_9^+$ ) (metastable 38.2). IR spectrum: 3000, 1780 ( $\gamma$ -lactone), 1725 (saturated ester), 1525, 1445, 1430, 1380, 1370, 1330, 1240 (acetate), 1145, 1100, 1015, 925  $cm^{-1}$ .

*Hydrogenolysis of product XI.* A mixture of product *XI* (180 mg), 20 ml of acetic acid, 80 mg of 30% Pd/C catalyst, and a crystal of *p*-toluenesulfonic acid was saturated with hydrogen for 3 days. After working up the mixture in a conventional manner a product (160 mg) was obtained which was chromatographed on silica gel (15 g) using benzene with 10% of ether for elution. In the first fractions a mixture of tetrahydroacetylismontanolid *VIII* and *IX*, m.p. 114–116°C and  $R_F$  0.6 (benzene-ether 4 : 1) appeared. Mass and IR spectra were identical with those of tetrahydroacetylismontanolid<sup>10</sup> (*IX*) and the mixture melting point with an authentic specimen was undepressed. In medium fractions a non-crystalline product was eluted, with  $R_F$  0.3 (benzene-

ether 1 : 1). Mass spectrum:  $m/e$  566, 506 (566 — 60), 446 (566 — 60 — 60), 404 (556 — 60 — 102), 288 (566 — 102 — 116 — 60), 228 (566 — 116 — 60 — 60), 85 ( $C_4H_9CO^+$ ), 57 ( $C_4H_9^+$ ) (metastable 38·2), 71 ( $C_4H_9O^+$ ). IR spectrum: 3 000, 2 900, 2 820, 1 780 ( $\gamma$ -lactone), 1 730 (saturated ester), 1 525, 1 460, 1 374, 1 335, 1 245 (acetate), 1 150, 1 100, 1 045, 1 020, 985, 935.

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