Structure of Epilubimin, Epioxylubimin, and Isolubimin, Spirovetivane Stress Metabolites in Diseased Potato[1)]

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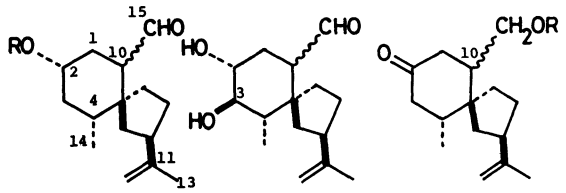
(Received December 3, 1981)

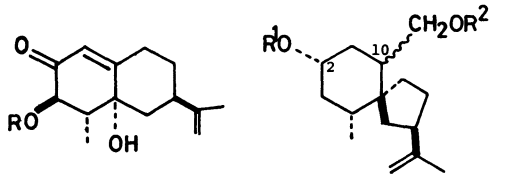
The isolation and structure elucidation of the title spirovetivane sesquiterpenes, stress metabolites produced in diseased potato tubers, are described.

In recent preliminary communications,[2,3)] we reported the isolation and structure of three spirovetivane sesquiterpenes named epilubimin (**1**), epioxylubimin (**2**), and isolubimin (**3**), stress metabolites produced in diseased potato tubers. In the present paper we describe details of the modified isolation procedure and structure elucidation of these metabolites.

Isolation. The metabolites were isolated from tuber tissues of potatoes (Rishiri, *Solanum tuberosum*×*S. demissum*) infected with an incompatible race of *Phytophthora infestans* as follows. Neutral chloroform extracts[4)] (83 g), obtained from the diseased potato tubers (300 kg), were roughly separated into five fractions (I—V) by chromatography. The fraction II (8.5 g) was again separated by chromatography to yield a "lubimin-rich" fraction (690 mg), containing epilubimin (**1**), isolubimin (**3**), and oxyglutinosone[5)] (**4**) beside lubimin[6)] (**5**) as its major component. This fraction was further separated by chromatography into "epilubimin-rich" and "oxyglutinosone and isolubimin-rich" fractions. Preparative TLC of the former gave **1** (59 mg), oil, $[\alpha]_D$ 0°, in pure state, and acetylation of the latter followed by preparative TLC afforded **4** and **3** as the respective acetates (**4a**)[5)] (43 mg) and (**3a**) (37 mg), mp 49—50 °C, $[\alpha]_D$ +26.3°. The latter acetate (**3a**) was hydrolyzed smoothly to give **3**, oil, $[\alpha]_D$ +34.4°, in pure state. On the other hand, the fraction IV (5.0 g), including oxylubimin[6)] (**6**) as its major constituent, contained two other metabolites, lubiminol[6)] (**7**) (=dihydrolubimin) and epioxylubimin (**2**). This was separated and purified by repeated chromatography and recrystallization to give **2** (294 mg), mp 123—124 °C, $[\alpha]_D$ −12.1°, in pure state.



1 10αH, R=H **2** 10αH, R=H **3** 10βH, R=H
1a 10αH, R=Ac **6** 10βH, R=H **3a** 10βH, R=Ac
5 10βH, R=H **9** 10αH, R=H
9a 10αH, R=Ac



4 R=H
4a R=Ac

7 10βH, $R^1=R^2=H$
7a 10βH, $R^1=H$, $R^2=Ac$
8 10αH, $R^1=R^2=H$
8a 10αH, $R^1=R^2=Ac$
8b 10αH, $R^1=H$, $R^2=Ac$

Epilubimin. Epilubimin (**1**) had the same molecular formula $C_{15}H_{24}O_2$ [*m/e* 236 (M^+)] as **5** and gave its monoacetate (**1a**), oil, $[\alpha]_D$ 0°. Hydride reduction of **1** afforded its dihydro derivative, epilubiminol[7,8)] (**8**), mp 135—136 °C, which also formed its diacetate (**8a**), oil. The mass, IR, and ^1H and ^{13}C NMR spectra of these compounds indicated the presence of the following structural units: $CH_3\dot{C}H$– [**1**, δ 0.94 (3H, d, J=6.5 Hz); **8**, 0.85 (3H, d, J=7 Hz)]: CH_2=C(CH_3)– [**1**, IR, 1640 and 891 cm^{-1}; δ 1.72 (3H, s) and 4.64(2H, s); **8**, IR, 1640 and 891 cm^{-1}; δ 1.68 (3H, s) and 4.64 (2H, s)]: –CHO [**1**, IR, 1715 cm^{-1}; δ 9.81 (1H, s),; **1a**, IR, no absorption near 3400 cm^{-1}; δ near 9.8]: –CH(OH)– [**1**, IR, 3300 cm^{-1}; δ 3.69 (1H, br, W_H=25 Hz); **1a**, IR, 1740 cm^{-1}; δ 4.64 (1H, br, W_H=25 Hz)]: a quaternary carbon atom (■)† of spiro type (**8**, δ 46.2, in Table 1). Addition of 0.25 mol equiv of the shift reagent Eu(dpm)$_3$ to the chloroform-*d* solution of **1** effected down-field shift of the ^1H NMR signals, leading to separation of most of the protons (Fig. 1), and spin-decoupling studies on the spectrum elucidated the following structural moiety: (■ ?)–CH(CH_3)–CH_2–CH(OH)–CH_2–CH(CHO ?)–(■). All the results strongly suggested that **1** would be an epimer (with an axial formyl group) of **5** (with an equatorial one). Compound **1** was treated with base under mild conditions to give a mixture of **1** and **5**, from which **5**, oil, $[\alpha]_D$ +31°, identical with natural lubimin, oil, $[\alpha]_D$ +36°, in the mass, IR, and ^1H NMR spectra, was isolated in 60% yield. Hence epilubimin is represented by formula **1**.

Epioxylubimin. Epioxylubimin (**2**) had the same molecular formula $C_{15}H_{24}O_3$ as **6**[6)] and displayed the mass spectrum similar closely to that of **6**. The IR, and ^1H and ^{13}C spectra (see Experimental and Table 1) indicated the presence of the following structural units: $CH_3\dot{C}H$–, CH_2=C(CH_3)–, two –CH(OH)–, –CH(CHO)–, and (■). While the ^1H NMR spectrum differed in multiplicity of the formyl methine protons from that of **6** [**2**, δ 9.87 (1H, s) and 2.41 (1H, t, J=4 Hz); **6**,[6)] δ 9.80 (1H, d, J=2.5 Hz) and 2.58 (1H, ddd, J=10, 4, and 2.5 Hz)], it also resembled as a whole closely to that of **6**. These facts, combined with the coocurrence of **1** and **5**, suggested that **2** would probably be a 10-epimer of **6**. Indeed, **2**, when treated with base, gave a mixture of **2** and **6** in 92% yield, from which

† The abbreviation denotes a carbon atom bearing no hydrogen atom.

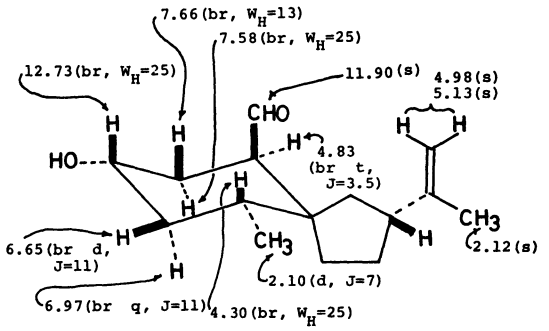


Fig. 1.

Table 1. The ^{13}C NMR spectra of epilubiminol (**8**), epioxylubimin (**2**), and isolubimin (**3**)[a]

Carbon No.	Chemical shift δ		
	8[b]	**2**	**3**[b]
1	42.1(42.1)	42.8	42.4(42.4)
2	66.0(66.6)	71.4	211.0(211.6)
3	40.0(40.4)	76.9	46.7(46.7)
4	35.2(35.4)	43.1	43.0(43.0)
5	46.2(46.4)	46.7	46.8(46.8)
6	35.2(34.0)	31.2	40.2(40.0)
7	47.8(47.9)	47.9	47.1(47.2)
8	31.1(31.2)	30.9 or 30.0	32.5(32.5)
9	31.1(31.3)	30.0 or 30.9	25.0(25.0)
10	48.9(49.1)	57.9	50.1(50.1)
11	147.9(148.4)	147.1	147.6(147.6)
12	107.8(108.2)	108.4	108.5(108.6)
13	21.3(21.5)	21.4	21.5(21.5)
14	17.1(17.2)	11.7	16.7(16.7)
15	61.2(62.1)	204.7	64.2(64.3)

a) Measured in chloroform-*d* at 25.2 MHz. b) The figures in the parentheses denote the chemical shifts reported by Stoessl *et al.*, *cf.*, Ref. 8.

6, mp 83—85 °C, $[\alpha]_D$ +52.6°, identical with natural oxylubimin, mp 85—86 °C, $[\alpha]_D$ +55.6°, was isolated in 60% yield.

Isolubimin and Epiisolubimin. Isolubimin (**3**), with the same molecular formula $C_{15}H_{24}O_2$ as that of **1**, exhibited the IR, ^1H and ^{13}C NMR spectra (Experimental and Tables 1 and 2), indicating the presence of the following structural units: CH_3CH–, CH_2=$C(CH_3)$–, $HOCH_2$–, O=$\overset{|}{C}$–, and (■). The structure of **3** was elucidated by correlation with **5** as follows. Lubiminol[6] (**7**), derived from **5**, was converted by treatment with acetic anhydride and pyridine in benzene into its 15-*O*-monoacetate (**7a**), oil, in 70% yield, which on Collins oxidation gave keto acetate in 60% yield, which was identified as acetylisolubimin (**3a**), in all respects. The same structure (**3**) had been proposed for "isolubimin" isolated from infected potato tubers independently by Kalan,[9] Stoessl,[8] and coworkers. In fact, the ^{13}C NMR spectrum of **3** was indistinguishable from that of Stoessl's isolubimin (Table 1).[10] However, the ^1H NMR spectrum appeared to be different from that reported by Kalan and Osman[9] (Table 2). Thus we prepared epiisolubimin (**9**), a 10-epimer of **3**, from epilbiuminol (**8**); namely, **8** underwent partial acetylation under the aforementioned conditions to give its 15-*O*-monoacetate (**8b**), $[\alpha]_D$ −9.0°, which on Collins oxidation afforded keto acetate (**9a**), oil, $[\alpha]_D$ −2.7°, isomeric from **3a**, in 60% yield. Interestingly, epiisolubimin (**9**), oil, obtained by hydrolysis of **9a**, exhibited the ^1H NMR spectrum, which resembled closely to that of "isolubimin" reported by Kalan and Osman (Table 2)[11].

Experimental

All the melting points were uncorrected. The purity of each compound was always checked by TLC over silica gel (Wakogel B-5 or Merck GF-254) with various solvent systems, and the spots were developed with cerium(IV) sulfate in dil sulfuric acid, iodine, and/or concd sulfuric acid. The optical rotations, UV, IR, and NMR (100 MHz) were measured in ethanol, in ethanol, in liquid state (oil) or in Nujol (crystals), and in chloroform-*d*, respectively, unless otherwise stated. The preparative TLC was carried out over silica gel (Merck GF-254), and the column chromatography over silca gel (Mallinckrodt AR-100) or silicic acid (Kiesel gel 60), respectively.

Isolation of Epilubimin (1), Epioxylubimin (2), and Isolubimin (3). The neutral chloroform extracts (83 g), corresponding to "neutral syrup" described in the section of "Isolation of rishitin,"[4] obtained from the diseased potato tubers (300 kg), were separated roughly into five fractions I—V by column chromatography over silica gel (1.8 kg), benzene, benzene–ethyl acetate (1 : 1), ether, ethyl acetate, and methanol being used as eluents, successively.

Fraction II (8.5 g), yellow oil, corresponding to "fraction E,"[4] was separated by chromatography over silica gel (100 g). Fractions (5.9 g) eluted with hexane–ethyl acetate (100 : 1) contained sterols as main components, which were not further examined. Successive elution with hexane–ethyl acetate (3 : 1) gave a "lubimin-rich" fraction (688 mg), which contained epilubimin (**1**), isolubimin (**3**), and oxyglutinosone (**4**) besides lubimin (**5**). This fraction was further separated into five fractions with hexane–ethyl acetate (5 : 1) as an eluent. Preparative TLC of the second fraction afforded epilubimin

Table 2. Comparison of the ^1H NMR spectra of isolubimin (**3**) and epiisolubimin (**9**) with that of Kalan's isolubimin (K–I)[a]

Proton	Chemical shift (δ) and splitting pattern (Hz)		
	3	**9**	K–I[b]
14-H	0.99(3H, d, J=7)	0.93(3H, d, J=6)	0.90(3H, d)
13-H	1.73(3H, s)	1.75(3H, s)	1.69(3H, s)
15-H	3.41(1H, dd, J=11, 8)	3.52(1H, dd, J=10, 8)	3.70(2H, m)
	3.85(1H, dd, J=11, 3)	3.79(1H, dd, J=10, 3)	
12-H	4.67(2H, s)	4.72(2H, s)	4.68(2H, s)

a) Measured in carbon tetrachloride at 100 MHz. b) Ref. 9.

(**1**) (59 mg), oil, $[\alpha]_D$ 0°, in pure state, showing a single spot on TLC; MS, *m/e* 236 (M^+), 218, 193, 175, 161, 149, 147, 145, 119, 107 (base), and 93; IR, 3300, 2730, 1715, 1640, and 891 cm^{-1}; ^1H NMR, δ 0.94 (3H, d, J=6.5 Hz), 1.72 (3H, s), 3.69 (1H, br, W_H=25 Hz), 4.64 (2H, br s), and 9.81 (1H, s). The third fraction, showing a single spot on TLC, was identified as slightly crude lubimin (**5**) (450 mg). The fifth, most polar fraction (160 mg) was an inseparable mixture of isolubimin and oxyglutinosone and treated with acetic anhydride and pyridine at room temperature overnight. The resulting acetate mixture (167 mg) was separated into two components by column chromatography over silica gel (4.0 g) with hexane–ethyl acetate (10 : 1) to give isolubimin acetate (**3a**) (37 mg), mp 49—50 °C, $[\alpha]_D$ +26.3°; MS, *m/e* 278 (M^+), 218, 203, 175, 146, 133, 107, 93, and 43 (base); IR, 1745, 1725, 1645, 1240, 1040, and 885 cm^{-1}; ^1H NMR, δ 1.00 (3H, d, J=6 Hz), 1.75 (3H, s), 2.04 (3H, s), 3.87 (1H, dd, J=11 and 9), 4.41 (1H, dd, J=11 and 3 Hz), and 4.73 (2H, s), and oxyglutinosone acetate[5] (**4a**) (43 mg) in pure state. The former (**3a**) was hydrolyzed to give isolubimin (**3**) as follows. A solution of **3a** (11 mg) in 50% aqueous methanol (2 ml) containing potassium carbonate (20 mg) was stirred at room temperature for 1 h under nitrogen. After removal of the solvent, the mixture was extracted with ether (25 ml), and the ether solution was washed with saturated brine (10 ml), dried and evaporated to leave an oily residue, which was purified by chromatography over silica gel with hexane–ethyl acetate (1 : 1) to give isolubimin (**3**) (8 mg) in pure state, oil, $[\alpha]_D$ +34.4°; MS, *m/e* 236 (M^+), 218, 205, 193, 175, 165, 149, 147, 135, 108 (base), and 93; IR, 3300, 3080, 1725, 1645, and 889 cm^{-1}; ^1H and ^{13}C NMR, in Tables 2 and 1.

Fraction IV (5.0 g), corresponding to "fraction H,"[4] was separated by column chromatography over silica gel (200 g), benzene and benzene–ethyl acetate mixtures being used as eluents. Fractions eluted with benzene–ethyl acetate (5 : 1) yielded a crystalline substance, which was recrystallized from diisopropyl ether to give epioxylubimin (**2**) (294 mg) in pure state, mp 123—124 °C, $[\alpha]_D$ −12.1°; MS, *m/e* 252 (M^+), 234, 219, 209, 191, 177, 165, 136, 135, 121, 107, and 93 (base); IR, 3390, 1720, 1640, and 893 cm^{-1}; ^1H NMR, δ 1.06 (3H, d, J=7Hz), 1.75 (3H, s), 2.411 H, d, J=4 Hz, 10-H), 3.08 (1H, t, J=9 Hz, 3-H), 3.49 (1H, dt, J=4 and 9 Hz, 2-H), 4.77 (2H, s) and 9.87 (1H, s): ^{13}C NMR, in Table 1. The follwing fractions eluted with benzene–ethyl acetate(3 : 1)gave oxylubimin[6] (**6**) (415 mg), mp 85—86 °C, $[\alpha]_D$ +55.6°. The more polar fractions eluted with benzene–ethyl acetate (2 : 1) afforded crystalline material (112 mg), showing a single spot, which on recrystallization from ether afforded lubiminol[6] (**7**) (dihydrolubimin), mp 129—130 °C, $[\alpha]_D$ +33°.

Acetylepilubimin (1a). Epilubimin (**1**) (25 mg) was treated with acetic anhydride (0.5 ml) and pyridine (0.5 ml) at room temperature for 14 h. The mixture was diluted with water and extracted with ether. The ether solution was washed with 1 M (1 M=1 mol dm^{-3}) hydrochloric acid, 5% aqueous sodium hydrogencarbonate, and saturated brine, dried, and evaporated to yield **1a** (26 mg), showing a single spot on TLC, oil, $[\alpha]_D$ 0°; MS, *m/e* 278 (M^+), 234, 218, 149 (base), 147, 107, 105, 93, and 91; IR, 1740, 1720, 1642, 1240, 1030, and 888 cm^{-1}; ^1H NMR, δ 0.96 (3H, d, J=7 Hz, 14-H), 1.71 and 1.95 (each 3H, s, 13-H and $OCOCH_3$), 4.64 (2H, s, 12-H), 4.64 (1H, br m, W_H=25 Hz, 2-H), and 9.78 (1H, s, 15-H).

Epilubiminol (8) and Its Diacetate (8a). A solution of **1** (20 mg) in methanol (2 ml) was stirred with sodium borohydride (50 mg) at room temperature for 6 h under nitrogen. After being diluted with water (10 ml), the mixture was extracted with ether. The ether solution was worked up as usual to give **8** (16 mg), mp 135—136 °C (from ether), $[\alpha]_D$ +3.4°; MS, *m/e* 238 (M^+), 220, 202, 177, 107, and 93; IR, 3400, 1640, 1030, 1010, and 891 cm^{-1}; ^1H NMR, δ 0.85 (3H, d, J=7 Hz, 14-H), 1.68 (3H, s, 13-H), 6.75 (3H, br m, 2- and 15-H), and 4.64 (2H, s, 12-H); ^{13}C NMR, in Table 1.

Compound **8** (25 mg) was treated with acetic anhydride (0.5 ml) and pyridine (0.5 ml) at room temperature for 16 h. The reaction mixture was worked up as usual to leave an oily residue (28 mg), which was purified by preparative TLC to give **8a** (22 mg), oil; MS, *m/e* 322 (M^+), 279, 262, 202 (base), 159, 107, and 93; IR, 1742, 1639, 1244, and 888 cm^{-1}; ^1H NMR, δ 0.89 (3H, d, J=7 Hz, 14-H), 1.69 (3H, s, 13-H), 1.90 and 1.97 (each 3H, s, $OCOCH_3$), 4.04 (2H, br m, W_H= 26 Hz, 15-H), 4.62 (2H, s, 12-H), and 4.64 (1H, br m, W_H= 25 Hz, 2-H); ^{13}C NMR, δ 16.8 and 20.9 (each q), 30.4, 31.1, and 31.5 (each t), 35.2 and 35.2 (each d), 36.0 and 41.3 (each t), 46.2 (s), 47.5 and 69.1(each d), 63.9 and 108.0(each t), and 147.3 (s).

Epimerization of Epilubimin (1) into Lubimin (5) and That of Epioxylubimin (2) into Oxylubimin (6). A solution of **1** (10 mg) in 5% methanolic potassium hydroxide (5 ml) was stirred at room temperature for 30 min under nitrogen. The reaction mixture was diluted with water (10 ml) and extracted repeatedly with ether (total 50 ml). The combined ether extracts were worked up as usual to leave an oily residue (11 mg), which was separated by column chromatography over silica gel. Elution with benzene–ether (5 : 1) gave the unchanged starting material (**1**) (3 mg) and its 10-epimer (**5**) (6 mg), oil, $[\alpha]_D$ +31°, which was identical with natural lubimin,[6] oil, $[\alpha]_D$ +36°, in the mass, IR, and ^1H NMR spectra.

Compound **2** (26 mg) was treated in the same manner as described above. The mixture, after being worked up as usual, left to oily substance (23 mg), which was separated by column chromatography over silica gal. Elution with benzene–ethyl acetate (1 : 1) gave the starting material (**2**) (6 mg) and its 10-epimer (**6**) (14 mg), mp 85—86 °C (from diisopropyl ether), $[\alpha]_D$ +52.6°, which was identical with natural oxylubimin,[6] mp 85—86 °C, $[\alpha]_D$ +55.6°, in the mass, IR, and ^1H NMR spectra.

Conversion of Lubimin (5) into Isolubimin (3). A solution of lubiminol[6] (**7**) (50 mg), obtained from **5**, in benzene (1 ml) was stirred with acetic anhydride (42 μl) and pyridine (0.2 ml) at room temperature for 5 h. The reaction mixture was mixed with methanol (1 ml) under cooling, stirred at room temperature for 10 min, and evaporated to leave an oily residue, which was extracted with ether (30 ml). The ether solution was worked up as usual to give an oily mixture (53 mg), which was separated into three fractions by chromatography over silica gel with benzene–ethyl acetate (1 : 1). Middle fractions gave crude 15-*O*-monoacetate (**7a**) (37 mg), showing a single spot on TLC, oil; ^1H NMR, δ 0.92 (3H, d, J=7 Hz, 14-H), 1.73 and 2.06 (each 3H, 13-H and $OCOCH_3$), 3.70 (1H, br, W_H=25 Hz, 2-H), 3.79 (1H, dd, J=11 and 9 Hz, 15-H), 4.35 (1H, dd, J=11 and 4 Hz), and 4.65(2H, s, 12-H). This was used for the next reaction without further characterization.

A solution of **7a** (37 mg) in dichloromethane (1 ml) was stirred with chromiun(VI) oxide (92 mg) and pyridine (68 μl) at room temperature for 30 min. The reaction mixture was mixed with ether (50 ml) and filtered. The filtrate was washed with 5% aqueous sodium hydrogencarbonate (15 ml) and saturated brine (15 ml), dried, and evaporated to yield oily substance (35 mg), which was purified by preparative TLC to give **3a** (28 mg), mp 45—48 °C, $[\alpha]_D$ +20.0°, identical with natural isolubimin acetate, mp 49—50 °C, $[\alpha]_D$ +26.3°, in the mass, IR, and ^1H NMR spectra.

Conversion of Epilubimin (1) into Epiisolubimin (9). A solution of epilubiminol (**8**) (19 mg), obtained from **1**, in benzene (20 μl) was treated with acetic anhydride (21 μl) and pyridine (60 μl) for 3 h at room temperature under stirring. The reaction mixture was mixed with methanol, stirred for 10 min, and evaporated to leave an oily residue, which was extracted with ether (30 ml). The ether solution was worked up as usual to give a colorless oil (22 mg), showing three spots on TLC, which was separated by column chromatography over silica gel. Elution with hexane–ethyl acetate (1 : 1) afforded diacetylepilubiminol (**8a**) (5 mg), the starting material (**8**) (2 mg), and 15-*O*-acetylepilubiminol (**8b**) (12 mg), oil, $[\alpha]_D$ −9.0°; MS, *m/e* 280 (M^+), 262, 220, 202, 187, 107 (base); IR, 3600, 3440, 3080, 1730, 1645, 1254, 1032, 1020, and 890 cm^{-1}; ^1H NMR, δ 0.89 (3H, d, J=6 Hz, 14-H), 1.71 (3H, s, 13-H), 2.05 (3H, s, $OCOCH_3$), 3.86 (1H, m, W_H= 20 Hz, 2-H), 4.12 (2H, d, J=7 Hz, 15-H), and 4.68 (2H, s, 12-H).

To a solution of pyridine (43 μl) and dichloromethane (1 ml) was added chromium(VI) oxide (30 mg), and the mixture was stirred for 15 min at room temperature under nitrogen. A solution of **8b** (12 mg) in dichloromethane (0.5 ml) was added into the above deep-red colored reaction mixture. After being stirred for 15 min, the mixture was diluted with ether (30 ml) and filtered. The ethereal filtrate was worked up as usual to leave an oily residue (12 mg), showing two spots on TLC, which was purified by preparative TLC over silica gel with hexane–ethyl acetate (10 : 1) to give the unreacted alcohol (**8b**) (3 mg) and acetylepiisolubimin (**9a**) (7 mg), oil, $[\alpha]_D$ −2.7°; MS, *m/e* 278 (M^+), 236, 218, 203 ,107, 105, 93, and 91; IR, 3090, 1735, 1712, 1646, 1238, 1034, and 895 cm^{-1}; ^1H NMR, δ 0.95 (3H, d, J=6 Hz, 14-H), 1.75 (3H, s, 13-H), 2.03 (3H, s, $OCOCH_3$), 3.86 (1H, dd, J=9 and 11 Hz, 15-H), 4.27 (1H, dd, J=3 and 11 Hz, 15-H), and 4.37 (2H, s, 12-H).

A solution of **9a** (5 mg) in methanol (1 ml) was stirred with potassium carbonate (5 mg) at room temperature for 1.5 h under nitrogen. The reaction mixture was diluted with ether (30 ml) and washed with water (10 ml) and saturated brine (10 ml), dried, and evaporated to give **9** (3 mg), oil; MS, *m/e* 236 (M^+), 218, 205, 149, 135, 107, 105 (base), 93, and 91; ^1H NMR, in Table 2.

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7) This compound must be the same as dihydroepilubimin, mp 138—140 °C, which was recently isolated from diseased potato tubers by Stoessl and coworkers, though direct comparison has not been carried out; *cf.*, Ref. 8.

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9) E. B. Kalan and S. F. Osman, *Phytochemistry*, **15**, 775 (1976).

10) The mass, IR, and ^1H NMR spectra of "isolubimin" isolated by Stoessl *et al.*[8] were not fully described.

11) Direct comparison of a Kalan's sample of isolubimin with our samples of isolubimin and epiisolubimin was not performed.