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# The Structure and Configuration of (+)-Glutionosone and (+)-Oxyglutinosone[1]

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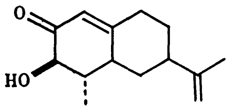
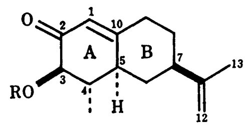
The structure elucidation of (+)-glutinosone and (+)-oxyglutinosone, antifungal norsesquiterpenes qualified as phytoalexins in diseased tobacco leaves and in diseased potato tubers, respectively, is described.

In recent preliminary communications[2,3] we reported the structure and configuration of (+)-glutinosone (**1**) and (+)-oxyglutinosone (**2**), antifungal norsesquiterpenes qualified as phytoalexins in diseased tobacco leaves and in diseased potato tubers, respectively. In the present paper we describe the details of the structure elucidation.

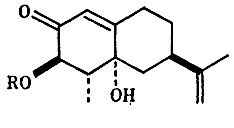
Glutinosone was isolated from leaves of *Nicotiana glutinosa* infected with tobacco mosaic virus and assigned formula **1′** by Burden and coworkers.[4] However, the disposition of an isopropenyl group and the configuration of all asymmetric centers have not completely been determined yet. The following transformation of rishitin (**3**) into (+)-glutinosone[5] has established that the relevant norsesquiterpene is represented correctly by formula **1**.



1′



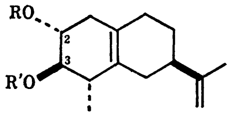
1 R=H
1a R=Ac



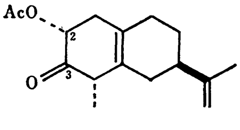
2 R=H
2a R=Ac

Treatment of (−)-rishitin[6] (**3**) with acetic anhydride (2.3 equiv) in a 1 : 20 mixture of pyridine and benzene (room temp, 5 h) followed by chromatography afforded the 2- and 3-monoacetates (**3a** and **3b**), mp 60.5—62.5 °C and 107—107.5 °C, in 34 and 23% yields, respectively, with the 2,3-diacetate[6] (**3c**, 5%) and the starting glycol (**3**, 35%) : **3a**, $\delta$ 3.31 (1H, t, $J$=8.5 Hz, 3-$\underline{\mathrm{H}}$) and 4.72 (3H, br, 2- and 12-$\underline{\mathrm{H}}$): **3b**, $\delta$ 3.62 (1H, do t, $J$= 6.5, 8.5, and 8.5 Hz, 2-$\underline{\mathrm{H}}$) and 4.60 (1H, t, $J$=8.5 Hz, 3-$\underline{\mathrm{H}}$). The 2- and 3-monoacetates (**3a** and **3b**), when oxidized with the Jones reagent in a heterogeneous mixture of ether and water (room temp, 16 and 21 h), were converted into the corresponding dehydro compounds, 3-oxo 2-acetate and 2-oxo 3-acetate (**4a** and **4b**), each oily, in 41 and 61% yields, respectively. In accordance with the assigned structures, the respective compounds (**4a** and **4b**) exhibited two strong absorption maxima at the carbonyl regions (**4a**, $\nu_{\max}$ 1757 and 1737 cm$^{-1}$; **4b**, $\nu_{\max}$ 1757 and 1744 cm$^{-1}$) and signals due to the protons at C-2 or C-3 [**4a**, $\delta$ 5.21 (1H, do d, $J$=11 and 8 Hz, 2-$\underline{\mathrm{H}}$); **4b**, $\delta$ 4.84 (1H, d, $J$=9 Hz, 3-$\underline{\mathrm{H}}$)] in the IR and NMR spectra.

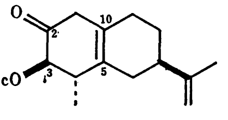
Transformation of the oxo acetates (**4b** and **4a**) into glutinosone (**1**) was undertaken under various conditions. Treatment of **4b** with base (KOAc in ethanol or alumina in dry benzene, room temp, 24 h) gave a complex mixture containing at least five compounds, while acid treatment (dil HCl in diglyme, room temp, 16 h) led to recovery of the starting material (**4b**). On the other hand, attempted isomerization of **4a** with base [NaOAc or $(CH_3)_4NOAc$ in water–ether, room temp, 45 h] failed, **4a** being recovered unchanged. One-step conversion of **3b** into **1** or **1a** under conditions of a modification[7] of the Oppenauer oxidation (aluminium isoproxide and *N*-methyl-4-piperidone, reflux, 5 h) also resulted only in hydrolysis of the acetoxyl group, giving **3**. The aimed transformation was achieved under most usual conditions; treatment of oxo acetate **4b** with base (KOH, 1.2 equiv) in methanol (room temp, 25 min) effected migration of the 5(10)-double bond with concomitant hydrolysis to give $\Delta^{1(10)}$-3-hydroxy 2-ketone (**1**), oily, in 46% yield, with the corresponding 3-acetate (**1a**, 41%), oily; **1**, $\lambda_{\max}$ 237 nm ($\varepsilon$ 14500); $\nu_{\max}$ 3470, 1676, 1645, and 1620 cm$^{-1}$; $\delta$ 3.79 (1H, d, $J$=12 Hz, 3-H) and 5.90 (1H, br s, $W_{\mathrm{H}}$=4 Hz, 1-$\underline{\mathrm{H}}$). All these spectra were identical with those of natural glutinosone[4] (**1**), establishing the



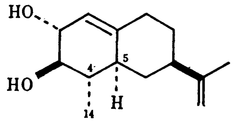
3 R=R′=H
3a R=Ac, R′=H
3b R=H, R′=Ac
3c R=R′=Ac



4a



4b



5

absolute configurations at C-3, C-4, and C-7 of (+)-glutinosone.[5]

Reduction of (+)-glutinosone (**1**) with sodium borohydride gave glycol[4] (**5**), mp 136—138 °C, in 44% yield. The NMR spectrum [δ 3.18 (1H, do d, $J$=10 and 8 Hz, 3-$\underline{H}$) and 4.06 (1H, br d, $J$=8 Hz, 2-$\underline{H}$)] indicated that the A ring existed in a half-chair conformation. Addition of 0.6 mol equiv of the shift reagent Eu(dpm)$_3$ effected complete separation of the NMR signals due to individual protons on the A ring, as shown in Fig. 1. Irradiation at δ 3.89 (14-H) collapsed a broad multiplet at 6.80 (4-H) into a slightly broad triplet ($J$=10 Hz), indicating the coupling constant between two protons at C-4 and C-5 to be 10 Hz. It follows that the proton in question at C-5 must be oriented axial (α-configuration) and hence (+)-glutinosone is represented by formula **1**.

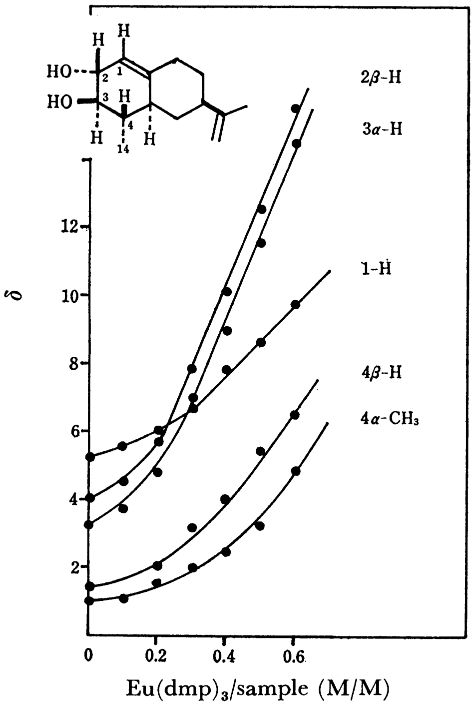


Fig. 1. Induced paramagnetic shifts for compound **5**.

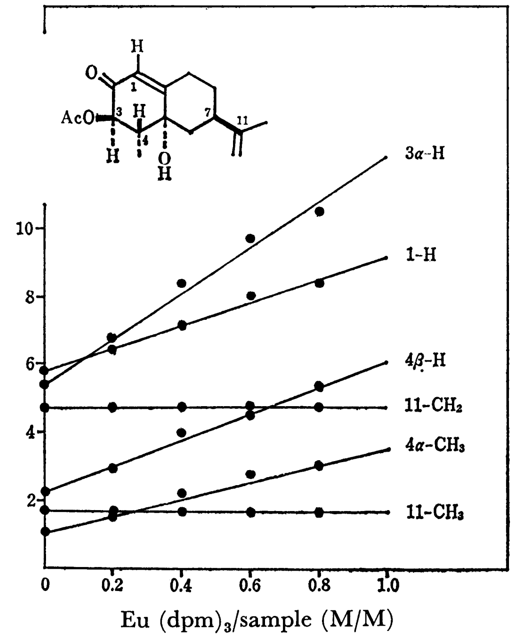


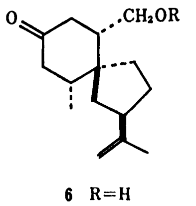
Fig. 2. Induced paramagnetic shifts for compound **2a**.

Oxyglutinosone (**2**) was isolated from tuber tissues of potatoes (*Solanum tuberosum* × *S. demissum*) infected by an incompatible race of *Phytophthora infestans* as follows. Neutral chloroform extracts (59 g), obtained from the diseased potato tubers (300 kg), were separated as described previously[6] to give "lubimin fraction" (Fraction E,[6] 4.7 g). This fraction was further purified by repeated chromatography to yield an oxyglutinosone and isolubimin-rich fraction (160 mg), with lubimin and epilubimin-rich fractions (174 and 110 mg), which on acetylation followed by preparative TLC over silica gel afforded oxyglutinosone (**2**) and isolubimin[3,8] (**6**) as the respective acetate (**2a**, 43 mg, and **6a**, 37 mg).

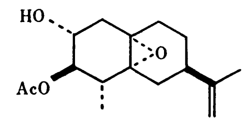
Oxyglutinosone acetate (**2a**), mp 99—101 °C and $[\alpha]_D$ +166°, was analyzed for $C_{16}H_{22}O_4$ [$m/e$ 278 ($M^+$)] and hydrolyzed in a 1 : 1 : 2 mixture of trimethylamine, water and methanol (room temp, 3 h) to give oxyglutinosone (**2**), oily and $[\alpha]_D$ +130°, in 56% yield after purification by preparative TLC. The UV, IR, and $^1$H-NMR spectra of these compounds indicated that oxyglutinosone (**2**) contained the following structural in units: a secondary methyl group [**2a**, δ 1.10 (3H, d, $J$=7 Hz)]: an isopropenyl [**2a**, $\nu_{max}$ 1642 (or 1638) and 897 cm$^{-1}$; δ 1.75 (3H, s) and 4.75 (2H, br s, $W_H$= 6 Hz)]: an α,β-unsaturated carbonyl [**2a**, $\lambda_{max}$ 230 nm (ε 12100); $\nu_{max}$ 1699 and 1638 (or 1642) cm$^{-1}$; δ 5.79 (1H, d, $J$=1.5 Hz, 1-$\underline{H}$)]: two (secondary and tertiary) hydroxyl groups [**2**, δ 4.10 (1H, d, $J$=12 Hz, 3-$\underline{H}$); **2a**, $\nu_{max}$ 3610, 3480, 1739, and 1240 cm$^{-1}$; δ 2.19 (3H, s) and 5.39 (1H, d, $J$=13 Hz, 3-$\underline{H}$)]. These spectra, coupled with spin-decoupling studies on the spectra in the presence of the shift reagent [Eu(dpm)$_3$, 0.2—0.8 mol equiv] (Fig. 2), indicating the existence of the following partial formula; (∗)-(CH$_3$)CH-CH-(OCOCH$_3$)-C(=O)-CH=(∗) in **2a**, in which (∗) denotes a quaternary carbon, suggesting that oxyglutinosone (**2**) would be a 5-hydroxy derivative of glutinosone (**1**). This was supported by comparison of the $^{13}$C-NMR spectra (Table 1) of both the 3-acetates

Table 1. The $^{13}$C-NMR spectra of glutinosone acetate (**1a**) and oxyglutinosone acetate (**2a**)

| Carbon No. | **1a** | **2a** |
|---|---|---|
| | Chemical shift (δ, CDCl$_3$, 25 MHz) | |
| 1 | 122.3 | 122.7 |
| 2 | 192.9 | 193.2 |
| 3 | 77.5 | 75.1 |
| 4 | 44.0 | 43.0 |
| 5 | 44.6 | 71.6 |
| 6 | 44.0 | 43.0 |
| 7 | 39.3 | 39.1 |
| 8 | 31.3 | 31.2 |
| 9 | 35.1 | 32.2 |
| 10 | 164.2 | 162.7 |
| 11 | 148.2 | 148.4 |
| 12 | 109.3 | 109.6 |
| 13 | 20.7 | 20.7 |
| 14 | 15.4 | 10.0 |



**6** R=H
**6a** R=Ac



**7**

(**1a** and **2a**) and confirmed as follows.

Rishitin 3-acetate (**3b**) was oxidized with *t*-butyl hydroperoxide in the presence of bis(acetylacetonato)-oxovanadium(IV)[9] [VO(acac)$_2$] to the 5α,10α-epoxide (**7**), mp 142—143 °C, in 83% yield. The α-configurational assignment to the epoxy group was deduced from the IR and $^1$H-NMR spectra; namely, (i) a broad absorption due to the hydrogen bond between the 2α-hydroxyl and epoxy groups was observed at 3480 cm$^{-1}$ in highly dilute carbon tetrachloride solution (0.0012 M, cell length, 50 mm), and (ii) a $^1$H-NMR signal due to the hydroxyl proton at δ 3.11 (1H, d, $J$=10 Hz) remained unchanged on dilution. The Collins oxidation of epoxide **7** followed by treatment with silica gel afforded hydroxy α,β-unsaturated ketone, mp 99—101 °C and [α]$_D$ +153°, in 54% yield, whose spectra (MS, UV, IR, and $^1$H-NMR) were identical with those of natural oxyglutinosone (**2a**). This transformation has established that oxyglutinosone (**2**) is 5α-hydroxyglutinosone.

## 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, Kieselgel GF-254) with various solvent systems, and the spots were developed with cerium(IV) sulfate in dil sulfuric acid, iodine, vaniline–sulfuric acid[6] and/or the Ehrlich reagent. The optical rotations, UV, IR, and NMR (100 MHz) spectra were measured in ethanol, ethanol, chloroform, and chloroform-*d*, unless otherwise stated. The abbreviations "s, d, t, q, m, br, and do" in the NMR spectra denote "singlet, doublet, triplet, quartet, multiplet, broad, and double," respectively. The preparative TLC was carried out over silica gel (Merck, Kieselgel GF-254) and the column chromatography over silica gel (Merck, Kieselgel 70—230 mesh).

*Partial Acetylation of Rishitin (3).* Compound **3** (3.09 g, [α]$_D$ −35.1°) was treated with acetic anhydride (3.0 ml) in benzene (80 ml) and pyridine (4 ml) at room temperature for 5 h under stirring. After addition of water, the mixture was separated into organic (benzene) and aqueous layers, and the latter was extracted with ether. The benzene and ether solutions were combined, washed with 2 M hydrochloric acid (HCl), 5% aq sodium hydrogencarbonate (NaHCO$_3$) and water, dried over anhydrous sodium sulfate and evaporated to leave resinous material (3.68 g), which was separated by column chromatography over silica gel (400 g), benzene–ether mixtures being used as solvents. Fraction eluted with benzene–ether (5: 1) afforded reshitin diacetate[6] (**3c**, 0.22 g), mp 68—70 °C (from hexane), which was identical with an authentic sample. Early fractions eluted with benzene–ether (4: 1) gave rishitin 2-acetate (**3a**, 1.25 g), mp 60.5—62.5 °C and [α]$_D$ −33.6°; MS, *m/e* 204 (base, M$^+$ −AcOH), 189, 186, 175, 171, and 161; IR, $\nu_{max}$ (Nujol) 3320, 3245, 3080, 1735, 1643, 1248, 1069, 1032, and 897 cm$^{-1}$; NMR, δ (CCl$_4$) 1.16 (3H, d, $J$=6.5 Hz, 14-H), 1.72 and 2.05 (each 3H, s, 13-H̲ and OCOCH̲$_3$), 3.31 (1H, t, $J$=8.5 Hz, 3-H), and 4.72 (3H, br, 2-H̲ and 12-H̲). Found: C, 72.82; H, 9.22%. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15%. Fractions eluted with benzene–ether (4: 1 and 3: 1) yielded rishitin 3-acetate (**3b**, 0.83 g), mp 107—107.5 °C (from hexane–diisopropyl ether) and [α]$_D$ −38.9°; MS, *m/e* 204 (base, M$^+$ −AcOH), 189, 186, 175, 171, and 161; IR, $\nu_{max}$ (Nujol) 3440, 3400, 3080, 1736, 1644, 1239, 1075, 1032, 1021, 1009, and 883 cm$^{-1}$; NMR, δ (CCl$_4$) 1.03 (3H, d, $J$=7 Hz, 14-H̲), 1.72 and 2.09 (each 3H, s, 13-H̲ and OCOCH̲$_3$), 3.62 (1H, do t, $J$=6.5, 8.5, and 8.5, 2-H̲), 4.60 (1H̲, t, $J$=8.5 Hz, 3-H̲), 4.60 and 4.68 (each 1H, br s, 12-H̲). Found: C, 68.37; H, 8.85%. Calcd for $C_{16}H_{24}O_3 \cdot H_2O$: C, 68.05; H, 9.28%. Fractions eluted with ethyl acetate gave rishitin (**3**, 1.07 g).

*Oxidation of 3a and 3b.* i) To a heterogeneous mixture of ether (5 ml) containing **3a** (52 mg) and water (2.5 ml) was added the Jones reagent (1 ml, 2.16 mmol) under stirring, and the mixture was further stirred vigorously at room temperature for 16 h. After dilution with ether, the mixture was separated into ether and aqueous layers, and the aqueous solution was extracted with ether. All the ether solutions were combined, washed with 5% aq sodium thiosulfate ($Na_2S_2O_3$), 5% aq NaHCO$_3$ and saturated brine, dried and evaporated to leave oil (44 mg), which was purified by chromatography over silica gel with benzene–ether (5: 1) to give 3-dehydrorishitin 2-acetate (**4a**, 24 mg), oily and [α]$_D$ +9.6°; MS, *m/e* 262 (M$^+$), 202, 187, 172, 159 (base), 134, 105, and 60; IR, $\nu_{max}$ (neat) 3070, 1757, 1737, 1643, 1231, 1019, and 889 cm$^{-1}$; NMR δ (CCl$_4$), 1.19 (3H, d, $J$=7.5 Hz, 14-H̲), 1.75 and 2.10 (each 3H, s, 13-H̲ and OCOCH̲$_3$), 2.92 (1H, q, $J$=7.5 Hz, 4-H̲), 4.67 and 4.73 (each 1H, br s, $W_H$=4.5 Hz, 12-H̲), and 5.21 (1H, do d, $J$=11 and 8 Hz, 2-H̲).

ii) Compound **3b** (159 mg) was oxidized with the Jones reagent (2.0 ml) in ether (16 ml) and water (7.5 ml) at room temperature for 21 h under stirring. The mixture was worked up as described above to leave an oily substance (159 mg), which was purified by chromatography over silica gel (8 g) with benzene–ether (5: 1) to give 2-dehydrorishitin 3-acetate (**4b**, 96 mg), oily and [α]$_D$ +59.4°; MS, *m/e* 262 (M$^+$), 202, 187, 159, (base), 134, 91, and 60; IR, $\nu_{max}$ (neat) 3080, 1757, 1744, 1643, 1226, 1050, and 889 cm$^{-1}$; NMR, δ (CCl$_4$) 1.14 (3H, d, $J$=7 Hz, 14-H̲), 1.74 and 2.10 (each 3H, s, 13-H̲ and OCOCH̲$_3$), 2.59 (1H, br, 4-H̲), 2.71 and 2.95 (each 1H, ABq, $J$=19 Hz, 1-H̲), 4.65 and 4.70 (each 1H, br s, $W_H$=4.5 Hz, 12-H̲), and 4.84 (1H, d, $J$=9Hz, 3-H̲). Fractions eluted with benzene–ether (3: 1) afforded the starting alcohol (**3b**, 29 mg).

*Transformation of 4b into 1a and 1.* To a methanol solution (2.0 ml) of **4b** (12.3 mg) was added 0.12 M potassium hydroxide in methanol (0.46 ml), and the whole solution was stirred at room temperature for 25 min under stirring. The solution was made acidic by addition of 3 M HCl and water, evaporated, and extracted with ethyl acetate (4×10 ml). The extracts were worked up as usual to leave oily residue (11.9 mg), which was separated into two fractions by preparative TLC over silica gel with benzene–ether (5: 1). A more mobile fraction gave an oily substance (5.0 mg), [α]$_D$ +64.8°, showing a single spot on TLC and the following spectra: MS, *m/e* 262 (M$^+$), 234, 202, 173, 162, 159, 147, 134, 131, 121, 94 (base), and 91; UV, $\lambda_{max}$ 236 nm (ε 15200); IR, $\nu_{max}$ 1748, 1692, 1643, 1627, 1228, and 895 cm$^{-1}$; NMR, δ 1.12 (3H, d, $J$=6 Hz, 14-H̲), 1.76 and 2.21 (each 3H, s, 13-H̲ and OCOCH̲$_3$), 4.74 (2H, br s, $W_H$=5 Hz, 12-H̲), 5.11 (1H, d, $J$=12 Hz, 3-H̲), and 5.86 (1H, br s, $W_H$=5 Hz, 1-H̲). These spectral data were completely identical with the reported of glutinosone acetate.[4] A less mobile (more polar) fraction afforded an oily substance (4.7 mg), $[\alpha]_D$ +57.2°, showing a single spot on TLC; MS, *m/e* 220 (M$^+$), 192, 191, 162, 147, 134, 121, and 94 (base); UV, $\lambda_{max}$ 237 nm ($\varepsilon$ 14500); IR, $\nu_{max}$ 3470, 1676, 1645, 1620, and 896 cm$^{-1}$; NMR, $\delta$ 1.23 (3H, d, $J=6$ Hz, 14-H), 1.73 (3H, s, 13-H), 3.72 (1H, s, OH), 3.79 (1H, d, $J=12$ Hz, 3-H), 4.72 (2H, br s, $W_H=5$ Hz, 12-H), and 5.90 (1H, br s, $W_H=4$ Hz, 1-H). These spectra were identical with the reported of glutinosone[4] (**1**). The latter (**1**, 3.6 mg), when treated with acetic anhydride (0.5 ml) and pyridine (1.0 ml) at room temperature for 14 h and then purified by chromatography over silica gel (1.0 g) with benzene–ether (1:1), was converted into the acetate (4.0 mg), whose spectral data were identical with those of **1a**.

*Hydride Reduction of 1.* Compound **1** (20.5 mg) was treated with sodium borohydride (16.0 mg) in ethanol (3.0 ml) at room temperature for 2.5 h under stirring. After addition of acetic acid, the mixture was evaporated and shaken with water and ethyl acetate (4×10 ml). The acetate solution was worked up as usual to leave crystalline residue (13.3 mg), which was purified by preparative TLC with ether and recrystallized from ethyl acetate–hexane to yield dihydroglutinosone (**5**, 9.0 mg), mp 136—138 °C (lit,[4] 129—132 °C) and $[\alpha]_D$ −29.6°; MS, *m/e* 222 (M$^+$), 204, 189, 176, 161, 133, 123, 121, 107, 105, 96 (base), 93, and 91; IR, $\nu_{max}$ 3580, 3400, 3070, 1643, 1069, 1047, 1041, and 894 cm$^{-1}$; NMR, $\delta$ 1.11 (3H, d, $J=6$ Hz, 14-H), 1.73 (3H, s, 13-H), 3.18 (1H, do d, $J=10$ and 8 Hz, 3-H), 4.06 (1H, br d, $J=8$ Hz, 2-H), 4.70 (1H, br s, $W_H=4$ Hz, 12-H), and 5.28 (1H, br s, $W_H=5$ Hz, 1-H).

*Isolation of Oxyglutinosone (2).* The fraction E (4.7 g), described in the section of "Isolation of rishitin,"[6] was separated roughly into two fractions, less polar epilubimin and lubimin-rich (2.50 g) and more polar oxylubimin and isolubimin-rich fractions (2.14 g), by chromatography over silica gel (200 g) with a 5:1 mixture of hexane and ethyl acetate mixture. The latter was further separated into less polar (158 mg), middle (688 mg) and polar fractions (773 mg) by chromatography over silica gel (100 g), hexane–ether mixtures (10:1—3:1) being used as solvents. The middle fraction was again submitted to chromatography over silica gel (50 g) with hexane and hexane–ethyl acetate mixtures to yield epilubimin-rich (110 mg), and oxyglutinosone and isolubimin-rich fractions (160 mg). The last fraction (160 mg) was treated lubimin-rich (174 mg) with acetic anhydride (1 ml) and pyridine (5 ml) at room temperature for 16 h. The reaction mixture was worked up as usual to give an oily substance (140 mg), showing two main spots on TLC, which was separated and purified by preparative TLC (3 plates) over silica gel. A less polar fraction gave isolubimin acetate[3,8] (**6a**, 37 mg) mp 49—51 °C (from diisopropyl ether) and $[\alpha]_D$ +34.4°, which a more polar fraction afforded oxyglutinosone acetate (**2a**, 43 mg), mp 101 °C (from diisopropyl ether) and $[\alpha]_D$ +166°; MS, *m/e* 278 (M$^+$), 260, 250, 218, 200, and 178 (base); UV, $\lambda_{max}$ 230 nm ($\varepsilon$ 12100); IR, $\nu_{max}$ 3610, 3480, 1739, 1699, 1642, 1638, 1240, and 897 cm$^{-1}$; NMR, $\delta$ 1.10 (3H, d, $J=7$ Hz, 14-H), 1.75 and 2.19 (each 3H, s, 13-H and OCOC$H_3$), 4.75 (2H, br s, $W_H=6$ Hz, 12-H), 5.39 (1H, d, $J=13$Hz, 3-H), and 5.79 (1H, d, $J=1.5$ Hz, 1-H).

The acetate (**2a**, 4 mg) was dissolved in a 1:1:2 mixture (2 ml) of triethylamine, water and methanol, and stirred at room temperature for 3 h. The solution was concentrated below 16 °C, and the residue was extracted with ether (20 ml). The ether solution was washed with saturated brine (10 ml), dried and evaporated to dryness to leave oily residue, showing two spots on TLC, which was separated by preparative TLC (1 plate) over silica gel to give the starting acetate (**2a**, 1.5 mg) and oxyglutinosone (**2**, 2.2 mg), oily and $[\alpha]_D$ +130°; MS, *m/e* 236 (M$^+$), 218, 200, and 178 (base); UV, $\lambda_{max}$ 230 nm ($\varepsilon$ 12100); IR, $\nu_{max}$ 3560, 3440, 1682, 1643, and 890 cm$^{-1}$; NMR, $\delta$ 1.25 (3H, d, $J=6$ Hz, 14-H), 1.74 (3H, s, 13-H); 4.10 (1H, d, $J=12$ Hz, 3-H), 4.73 (2H, br s, $W_H=7$ Hz, 12-H), and 5.89 (1H, d, $J=1.5$ Hz, 1-H).

*Conversion of 3b into 2a.* i) Compound **3b** (85 mg) was oxidized with *t*-butyl hydroperoxide (0.1 ml) in the presence of VO(acac)$_2$ (2 mg) in benzene (1.2 ml) under reflux for 10 min. After being cooled, the mixture was stirred with 5% aq sodium hydrogensulfite (NaHSO$_3$, 3 ml) at room temperature for 1 h. The benzene solution, after being separated from the aqueous solution, was washed with 5% aq NaHSO$_3$ (10 ml), 5% aq NaHCO$_3$ (10 ml) and saturated brine (10 ml), dried and evaporated to leave crystalline residue (75 mg), which was recrystallized from diisopropyl ether to give 5α,10α-epoxyrishitin 3-acetate (**7**, 75 mg), mp 140—143 °C and $[\alpha]_D$ −14°; IR, $\nu_{max}$ (Nujol) 3480, 1730, 1640, 1240, 1037, and 893 cm$^{-1}$; NMR, $\delta$ 1.27 (3H, d, $J=6$ Hz, 14-H), 1.71 and 2.07 (each 3H, s, 13-H and OCOC$H_3$), 3.11 (1H, d, $J=10$ Hz, OH), 3.69 (1H, do q, $J=10$, 5, 5, and 5 Hz, 2-H), and 4.70 (3H, br m, 3- and 12-H).

ii) To a suspended mixture of chromium(VI) oxide (70 mg) in dry pyridine (0.14 ml) and dichloromethane (2 ml) was added **7** (28 mg) in dichloromethane (0.4 ml) under stirring, and the whole mixture was stirred vigorously at room temperature for 15 min. The mixture was diluted with ether 30 ml) and filtered. The filtrate was washed with 5% aq NaHCO$_3$ and saturated brine, dried and evaporated to leave oily residue (21 mg), showing two spots on TLC. The residue was dissolved in chloroform (1 ml), put on front lines of silica gel plates (Merck, DC-Alufolien Kieselgel 60 F-254, 20×20 cm$^2$, 3 plates) for 20 min, and developed with a 1:1 mixture of ethyl acetate and hexane. A fraction showing an UV spectrum was extracted with ethyl acetate to give **2a** (15 mg), mp 99—101 °C and $[\alpha]_D$ +153°, whose spectra (MS, UV, IR, and $^1$H-NMR) were identical with the corresponding of natural oxyglutinosone acetate (**2a**).

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