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Studies on Shikon. III.[1] New Furylhydroquinone Derivatives, Shikonofurans A, B, C, D and E, from *Lithospermum erythrorhizon* Sieb. *et* Zucc.

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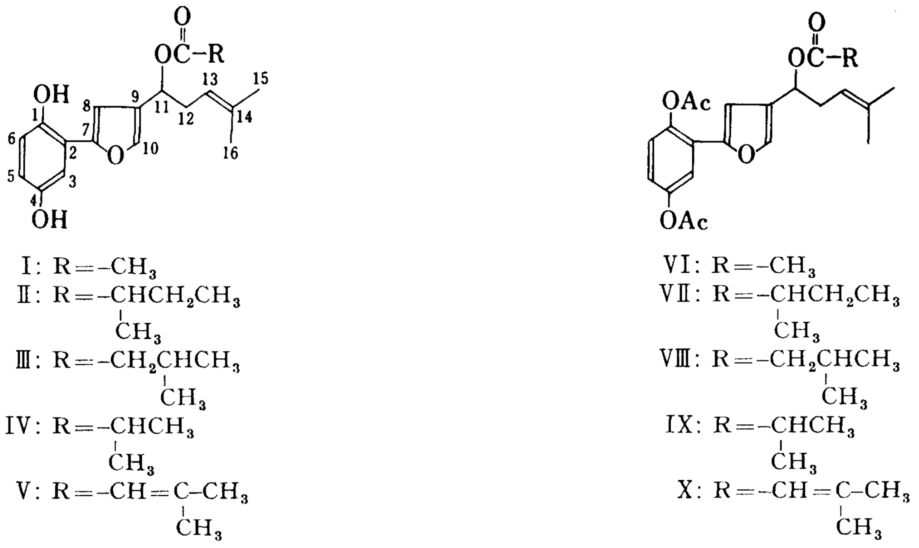
Five new furylhydroquinone derivatives, named shikonofurans A, B, C, D and E, were found in the root of *Lithospermum erythrorhizon* Sieb. *et* Zucc. (Boraginaceae). Shikonofuran A was proved to have the structure I, shown in Chart 1, by direct comparison of the spectral data of its diacetate with those of echinofuran leucoacetate. The structures of the other compounds were established on the basis of spectral and chemical evidence as II, III, IV and V, shown in Chart 1.

Keywords——*Lithospermum erythrorhizon*; Boraginaceae; shikonofurans A, B, C, D and E; furylhydroquinone derivatives; preparative high-speed liquid chromatography

In the previous papers we reported the isolation and structural elucidation of lithospermidins A and B,[2] new naphthoquinone derivatives, as pigments and caffeic acid esters[1] as colorless substances in the roots of *Lithospermum erythrorhizon* Sieb. *et* Zucc. (Boraginaceae; Japanese name, as the drug, 'Koh-shikon'). In further studies on this plant, we have isolated new furylhydroquinone derivatives, shikonofurans A, B, C and a mixture of D and E, and we report here the structures of these colorless substances.

Shikonofuran A (I) was isolated as colorless needles, mp 74—76°C, $C_{18}H_{20}O_5$ (m/z 316, M^+), $[\alpha]_D$ $-50.0°$, positive Ehrlich test. The ultraviolet (UV) spectrum exhibited absorption maxima at 235 (sh) (3.89), 265 (sh) (4.09), 270.5 (4.18), 281.5 (4.09), 326.5 (3.94) and 337 (sh) (3.88) nm (log ε). The circular dichroism (CD) spectrum showed a negative Cotton effect $[\theta]$ -305 (335 nm). The infrared (IR) spectrum suggested the presence of hydroxyl groups (3390 cm^{-1}) and an ester (1710 and 1250 cm^{-1}). The proton nuclear magnetic resonance (NMR) spectrum of I showed signals at δ 1.63, 1.70 (each 3H, s), 2.07 (3H, s), 2.55 (2H, t, $J=7$ Hz), 5.06 (1H, br t, $J=7$ Hz) and 5.74 (1H, t, $J=7$ Hz). These observations indicated the presence of the same side chain as that of acetylshikonin (XI)[2] in I. The signals could be assigned to isopropylidene methyl groups, an acetoxyl group, allyl methylene protons, a vinyl proton and a proton joined with the carbon bearing the acetoxyl group, respectively. In the aromatic proton region, signals due to five protons [δ 6.64 (dd, $J=2.5$ and 9 Hz), 6.71 (s), 6.83 (dd, $J=0.8$ and 9 Hz), 7.00 (dd, $J=0.8$ and 2.5 Hz) and 7.44 (br s)] were observed. Acetylation of I with acetic anhydride and anhydrous sodium acetate gave the diacetate (VI), colorless oil, $C_{22}H_{24}O_7$ (m/z 400, M^+). The NMR spectrum of VI exhibited a typical ABM pattern [δ 6.95 (1H, dd, $J=2.5$ and 9 Hz), 7.14 (1H, dd, $J=0.8$ and 9 Hz) and 7.50 (1H, dd, $J=0.8$ and 2.5 Hz)] besides two signals [δ 6.70 (1H, br s) and 7.42 (1H, br s)] in the aromatic proton region. On the basis of the signals at δ 6.71 and 7.44 and the IR absorption at 870 cm^{-1}, it could be deduced that an α',β-disubstituted furan ring was present in I. To consider all of these actual facts, I can be regarded as a furylhydroquinone derivative having the same side chain as XI. A few furylbenzoquinone derivatives have been found as pigments in the family Boraginaceae.[3,4] Recently, echinofuran (XVI) was isolated as a pigment from the callus cultures of *Echium lycopsis*[5] (Boraginaceae). Reductive acetylation of XVI with zinc–acetic anhydride–pyridine mixture gave echinofuran leucoacetate[5] which was found to be identical



I: $R=-CH_3$
II: $R=-\underset{CH_3}{CH}CH_2CH_3$
III: $R=-CH_2\underset{CH_3}{CH}CH_3$
IV: $R=-\underset{CH_3}{CH}CH_3$
V: $R=-CH=\underset{CH_3}{C}-CH_3$

VI: $R=-CH_3$
VII: $R=-\underset{CH_3}{CH}CH_2CH_3$
VIII: $R=-CH_2\underset{CH_3}{CH}CH_3$
IX: $R=-\underset{CH_3}{CH}CH_3$
X: $R=-CH=\underset{CH_3}{C}-CH_3$

Chart 1

with shikonofuran A diacetate. Thus, the structure of shikonofuran A was determined as dihydroechinofuran, *i.e.*, structural formula I in Chart 1.

Shikonofurans B (II), C (III), D (IV) and E (V) were purified as a mixture and exhibited a positive Ehrlich test. The NMR spectral properties of the mixture in the aliphatic proton region closely resembled those of a mixture[8] of α-methyl-*n*-butyrylshikonin (XII),[2] isovalerylshikonin (XIII),[2] isobutyrylshikonin (XIV)[6] and β,β-dimethylacryloylshikonin (XV).[6-8] Accordingly, separation by preparative high-speed liquid chromatography (PHLC) was attempted. After several investigations, μ-Bondapak Phenyl and water–tetrahydrofuran (60: 40) were selected as the column material and the eluent, respectively. The elution profile of the mixture (II, III, IV and V) on PHLC is shown in Fig. 1.

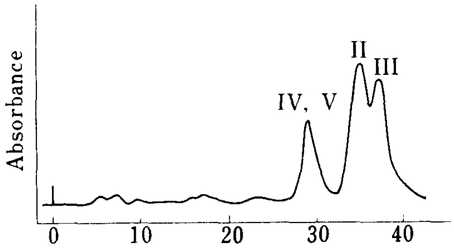


Fig. 1. Chromatogram obtained by PHLC of the Fraction containing II, III, IV and V

Column, μ-Bondapak Phenyl (7.8 mm × 30 cm); mobile phase, H_2O–THF (60: 40); flow rate 4 ml/min; detector, UV at 280 nm.

Compound II, $C_{21}H_{26}O_5$ (m/z 358, M^+), $[\alpha]_D$ $-33.3°$, is a colorless oil and showed a negative Cotton effect $[\theta]$ -439 (335 nm). Its NMR spectrum closely resembled that of XII[2] except in the aromatic region. The signals could be assigned to an α-methyl-*n*-butyryl group [δ 0.88 (3H, t, $J=7$ Hz), 1.16 (3H, d, $J=7$ Hz) and 2.44 (1H, m)], isopropylidene methyl groups [δ 1.63 (3H, s) and 1.70 (3H, s)], allyl methylene protons [δ 2.57 (2H, t, $J=7$ Hz)], a vinyl proton [δ 5.08 (1H, br t, $J=7$ Hz)] and a proton linked with the carbon bearing the α-methyl-*n*-butyryloxyl group [δ 5.78 (1H, t, $J=7$ Hz)]. Signals in the aromatic region were exactly the same as those of I. Namely, signals of the α'- and β-protons of the furan ring [δ 7.43 (1H, br s) and 6.70 (1H, s)] and protons of monosubstituted hydroquinone [δ 6.64 (1H, dd, $J=2.5$ and 9 Hz), 6.83 (1H, dd, $J=0.8$ and 9 Hz) and 6.99 (1H, dd, $J=0.8$ and 2.5 Hz)] were observed. Taking into consideration the IR and UV spectra and formation of the diacetate (VII, colorless oil), the structure of shikonofuran B was formulated as II in Chart 1.

Compound III, $C_{21}H_{26}O_5$ (m/z 358, M^+), $[\alpha]_D$ $+60.0°$, $[\theta]$ -376 (337 nm), was obtained as a colorless oil. Acetylation of III in the usual manner gave the diacetate VIII, colorless oil. The NMR signals of III were quite similar to those of XIII[2] except in the aromatic region.

XI: $\mathrm{R}=-\mathrm{CH_3}$

XII: $\mathrm{R}=-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2CH_3}$

XIII: $\mathrm{R}=-\mathrm{CH_2}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_3}$

XIV: $\mathrm{R}=-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_3}$

XV: $\mathrm{R}=-\mathrm{CH}=\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}-\mathrm{CH_3}$

XVI

Chart 2

The signals were assignable to isovaleryl methyl groups [δ 0.95 (6H, d, $J=7$ Hz)], isopropylidene methyl groups [δ 1.63 (3H, s) and 1.69 (3H, s)], an isovaleryl methine proton [δ 1.96 (1H, m)], allyl methylene protons [δ 2.56 (2H, t, $J=7$ Hz)], a vinyl proton [δ 5.08 (1H, br t, $J=7$ Hz)] and a proton linked with the carbon bearing the isovaleryloxyl group [δ 5.78 (1H, t, $J=7$ Hz)], respectively. Signals in the aromatic region were the same as those of I and II. On the basis of these and the other spectral data, the structure of shikonofuran C was assigned as III, shown in Chart 1.

Compounds IV and V, purified in minute amounts as an inseparable oily mixture by PHLC, displayed UV and IR spectra similar to those of I, II and III. The high-resolution mass (high-MS) spectrum showed molecular ion peaks at m/z 344 ($C_{20}H_{24}O_5$) and 356 ($C_{21}H_{24}O_5$) and the MS spectrum of the diacetate (mixture of IX and X, colorless oil) exhibited ion peaks at m/z 428 (M^+) and 440 (M^+). The NMR spectrum of the mixture in the aromatic region showed exactly the same pattern as those of I, II and III. The other signals indicated the presence of the same side chains as those of XIV and XV. The signal could be assigned as follows: isobutyryl methyl groups [δ 1.15 (d, $J=7$ Hz) and 1.19 (d, $J=7$ Hz)], isopropylidene methyl groups [δ 1.62 (s) and 1.69 (s)], dimethylacryloyl methyl groups [δ 1.90 (s) and 2.16 (s)], allyl methylene protons [δ 2.55 (t, $J=7$ Hz)], a vinyl proton [δ 5.07 (br t, $J=7$ Hz)], an acryloyl vinyl proton [δ 5.60 (m)] and a proton linked with the carbon bearing the ester groups [δ 5.75 (t, $J=7$ Hz)]. All of these data indicated that the mixture contained two components, shikonofurans D and E, described by the structural formulae IV and V in Chart 1. However, the complete separation of these compounds has not yet been achieved.

Shikonofurans A, B and C showed negative first Cotton effects. Although we could not determine these [θ] values close to that of alkannin, [θ] -5070 (357 nm),[5] the negative sign and small [θ] values suggested these compounds consist of both enantiomers, with the (11-*S*)-enantiomers slightly dominant, as is accepted for echinofuran.

These new furylhydroquinone derivatives are very interesting in relation to the biosynthesis of naphthoquinone pigments.

Experimental

Materials were purchased from Nakaikohshindo (Kobe). Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations and CD spectra were taken with a Union PM-101 automatic polarimeter and a JASCO J-400X spectropolarimeter at 28°C, respectively. Hitachi model 200-20 and Shimadzu IR-430 spectrophotometers were used for the measurements of UV and

IR spectra, respectively. High-MS and field desorption mass (FD-MS) spectra were taken on a JEOL JMS-01SG-2 mass spectrometer. NMR spectra were recorded with a JEOL JNM-FX-60 spectrometer and chemical shifts are given in δ (ppm) with tetramethylsilane as an internal standard (s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet). PHLC conditions were as follows: high pressure machine with model 6000A solvent delivery system (Waters Associates, Inc.) and model 440 absorbance detector (Waters Associates, Inc., monitored at 280 nm); column, μ-Bondapak Phenyl (7.8 mm × 30 cm, stainless steel column); mobile phase, water–tetrahydrofuran (60: 40); flow rate, 4.0 ml/min; room temperature. Silica gel column chromatography was carried out with silicic acid (Mallinckrodt, 100 mesh)-Celite 545 (2: 1, in v/v).

Isolation——The roots of *Lithospermum erythrorhizon* SIEB. *et* ZUCC. (1800 g) were extracted three times with ether (10 l) at room temperature. After removal of the ether *in vacuo*, the extract (60 g) was column-chromatographed on Sephadex LH-20 (100 g) using hexane–methylene chloride and methylene chloride–acetone as eluents.

Fractions 1, 2 and 3 were obtained. Fraction 3 (6 g) was column-chromatographed on silicic acid (50 g). The fraction eluted with hexane–acetone (4: 1) was also rechromatographed on silicic acid (22 g) using hexane–ether (9: 1) and (4: 1) as eluents to give a mixture of II, III, IV and V (240 mg) and crude I, respectively. Crude I was further purified by column chromatography (silicic acid), then recrystallized and 100 mg of the mixture was purified twice by PHLC to give II, III and a mixture of IV and V.

Shikonofuran A (I)——Recrystallization from methylene chloride furnished colorless needles, mp 74—76°C, 140 mg. $[\alpha]_D$ −50.0° (c = 0.52, $CHCl_3$). High-MS for $C_{18}H_{20}O_5$: Calcd *m/z* 316.1310; Found *m/z* 316.1330. CD (c = 0.023, MeOH) $[\theta]$ (nm): −305 (335), −339 (323), −1321 (281), −1219 (271), −677 (260) (sh) (negative maximum), +576 (237) (positive maximum). UV λ_{max}^{EtOH} nm (log ε): 235 (sh) (3.89), 265 (sh) (4.09), 270.5 (4.18), 281.5 (4.09), 326.5 (3.94), 337 (sh) (3.88). IR ν_{max}^{KBr} cm^{-1}: 3390, 1710, 1505, 1440, 1370, 1250, 1190, 1025, 870. NMR (in $CDCl_3$) δ: 1.63, 1.70 (each 3H, s, $=C-CH_3 \times 2$), 2.07 (3H, s, $-OCOCH_3$), 2.55 (2H, t, J = 7 Hz, $-CH_2-$), 5.06 (1H, br t, J = 7 Hz, $-CH=$), 5.74 (1H, t, J = 7 Hz, $-CH-OCO-$), 6.36 (1H, br s, $-OH$), 6.64 (1H, dd, J = 2.5 Hz, 9 Hz, C_5-H), 6.71 (1H, s, C_8-H), 6.83 (1H, dd, J = 0.8 Hz, 9 Hz, C_6-H), 7.00 (1H, dd, J = 0.8 Hz, 2.5 Hz, C_3-H), 7.44 (1H, br s, $C_{10}-H$).

Acetylation of I——Anhydrous sodium acetate (200 mg) was added to a solution of I (40 mg) in acetic anhydride (2 ml). The mixture was stirred at 50°C for 90 min, then worked up as usual. Purification by column chromatography (silica gel) gave the diacetate of I (VI) as a colorless oil, 44 mg. FD-MS *m/z*: 400 (M^+). UV λ_{max}^{EtOH} nm: 280. IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 1765, 1735, 1495, 1370, 1235, 1200, 1170, 1030, 915. NMR (in $CDCl_3$) δ: 1.61, 1.70 (each 3H, s, $=C-CH_3 \times 2$), 2.06, 2.31, 2.38 (each 3H, s, $-OCOCH_3 \times 3$), 2.55 (2H, br t, J = 7 Hz, $-CH_2-$), 5.05 (1H, br t, J = 7 Hz, $-CH=$), 5.72 (1H, t, J = 7 Hz, $-CH-OCO-$), 6.70 (1H, br s, C_8-H), 6.95 (1H, dd, J = 2.5 Hz, 9 Hz, C_5-H), 7.14 (1H, dd, J = 0.8 Hz, 9 Hz, C_6-H), 7.42 (1H, br s, $C_{10}-H$), 7.50 (1H, dd, J = 0.8 Hz, 2.5 Hz, C_3-H).

Shikonofuran B (II)——Obtained as a colorless oil, 25 mg. $[\alpha]_D$ −33.3° (c = 0.48, $CHCl_3$). High-MS for $C_{21}H_{26}O_5$: Calcd *m/z* 358.1779; Found: *m/z* 358.1752. CD (c = 0.016, MeOH) $[\theta]$ (nm): −439 (335), −548 (327), −1370 (280), −1261 (271), −932 (265) (sh) (negative maximum), +1178 (240) (positive maximum). UV λ_{max}^{EtOH} nm: 234 (sh), 265 (sh), 270.5, 282, 326.5, 337. IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 3380, 1700, 1510, 1440, 1200, 1025, 870. NMR (in $CDCl_3$) δ: 0.88 (3H, t, J = 7 Hz, $-CH_2C\underline{H}_3$), 1.16 (3H, d, J = 7 Hz, $-CH-C\underline{H}_3$), 1.63, 1.70 (each 3H, s, $=C-CH_3 \times 2$), 2.44 (1H, m, $-CO-CH-$), 2.57 (2H, t, J = 7 Hz, $-C\underline{H}_2-CH=$), 5.08 (1H, br t, J = 7 Hz, $-CH=$), 5.78 (1H, t, J = 7 Hz, $-CH-OCO-$), 6.43 (1H, br s, $-OH$), 6.64 (1H, dd, J = 2.5 Hz, 9 Hz, C_5-H), 6.70 (1H, s, C_8-H), 6.83 (1H, dd, J = 0.8 Hz, 9 Hz, C_6-H), 6.99 (1H, dd, J = 0.8 Hz, 2.5 Hz, C_3-H), 7.43 (1H, br s, $C_{10}-H$). PHLC (t_R, min): *ca.* 35.

Shikonofuran B Diacetate (VII)——Acetylation of II (9 mg) in a manner similar to that described above gave the diacetate (VII) as a colorless oil, 6 mg. FD-MS *m/z* 442 (M^+). UV λ_{max}^{EtOH} nm: 280. IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 1765, 1730, 1495, 1370, 1210, 1195, 1170, 1030, 915. NMR (in $CDCl_3$) δ: 0.87 (3H, t, J = 7 Hz, $-CH_2-C\underline{H}_3$), 1.14 (3H, d, J = 7 Hz, $-CH-C\underline{H}_3$), 1.63, 1.70 (each 3H, s, $=C-CH_3 \times 2$), 2.32, 2.37 (each 3H, s, $-OCOCH_3$), 2.55 (2H, t, J = 7 Hz, $-C\underline{H}_2-CH=$), 5.09 (1H, br t, J = 7 Hz, $-CH=$), 5.76 (1H, t, J = 7 Hz, $-CH-OCO-$), 6.70 (1H, br s, C_8-H), 6.97 (1H, dd, J = 2.5 Hz, 9 Hz, C_5-H), 7.15 (1H, dd, J = 0.8 Hz, 9 Hz, C_6-H), 7.41 (1H, br s, $C_{10}-H$), 7.51 (1H, dd, J = 0.8 Hz, 2.5 Hz, C_3-H).

Shikonofuran C (III)——Isolated as a colorless oil, 20 mg. $[\alpha]_D$ +60.0° (c = 0.30, $CHCl_3$). High-MS for $C_{21}H_{26}O_5$: Calcd *m/z* 358.1779; Found *m/z* 358.1755. CD (c = 0.017, MeOH) $[\theta]$ (nm): −376 (337), −215 (325) (sh), −618 (285), −322 (270) (negative maximum), +779 (247) (positive maximum). UV λ_{max}^{EtOH} nm: 234 (sh), 265 (sh), 270.5, 282, 326.5, 337. IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 3370, 1700, 1510, 1440, 1195, 1025, 870. NMR (in $CDCl_3$) δ: 0.95 (6H, d, J = 7 Hz, $-CH-C\underline{H}_3 \times 2$), 1.63, 1.69 (each 3H, s, $=C-CH_3 \times 2$), 1.96 (1H, m, $-CH_2-C\underline{H}-$), 2.18 (2H, m, $-CO-CH_2-$), 2.57 (2H, t, J = 7 Hz, $-C\underline{H}_2-CH=$), 5.08 (1H, br t, J = 7 Hz, $-CH=$), 5.78 (1H, t, J = 7 Hz, $-CH-OCO-$), 6.40 (1H, br s, $-OH$), 6.64 (1H, dd, J = 2.5 Hz, 9 Hz, C_5-H), 6.71 (1H, s, C_8-H), 6.83 (1H, dd, J = 0.8 Hz, 9 Hz, C_6-H), 7.00 (1H, dd, J = 0.8 Hz, 2.5 Hz, C_3-H), 7.44 (1H, br s, $C_{10}-H$). PHLC (t_R, min): *ca.* 37.

Shikonofuran C Diacetate (VIII)——Acetylation of III (10 mg) with acetic anhydride (0.5 ml) in pyridine (0.5 ml) at room temperature (overnight) gave the colorless noncrystalline diacetate (VIII), 5 mg. FD-MS *m/z*: 442 (M^+). UV λ_{max}^{EtOH} nm: 280. IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 1765, 1730, 1490, 1370, 1210, 1195, 1170, 1030, 915.

NMR (in $CDCl_3$) δ: 0.94 (6H, d, $J=7$ Hz, $-CH-C\underline{H}_3\times 2$), 1.63, 1.69 (each 3H, s, $=C-CH_3\times 2$), 2.15 (2H, m, $-CO-CH_2-$), 2.31, 2.38 (each 3H, s, $-OCOCH_3$), 2.55 (2H, t, $J=7$ Hz, $-C\underline{H}_2-CH=$), 5.07 (1H, br t, $J=7$ Hz, $-CH=$), 5.75 (1H, t, $J=7$ Hz, $-CH-OCO-$), 6.70 (1H, br s, C_8-H), 6.97 (1H, dd, $J=2.5$ Hz, 9 Hz, C_5-H), 7.15 (1H, dd, $J=0.8$ Hz, 9 Hz, C_6-H), 7.42 (1H, br s, $C_{10}-H$), 7.51 (1H, dd, $J=0.8$ Hz, 2.5 Hz, C_3-H).

Shikonofurans D (IV) and E (V)——Obtained as a mixture, colorless oil, 12 mg. High-MS for $C_{20}H_{24}O_5$: Calcd *m/z* 344.1622; Found *m/z* 344.1641; $C_{21}H_{24}O_5$: Calcd *m/z* 356.1622; Found *m/z* 356.1605. UV λ_{max}^{EtOH} nm: 265 (sh), 270.5, 282, 326, 336 (sh). IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 3380, 1700, 1510, 1440, 1200, 1160, 870. NMR (in $CDCl_3$) δ: 1.15, 1.19 (each d, $J=7$ Hz, $-CH-C\underline{H}_3\times 2$), 1.62, 1.69 (each s, $=C-C\underline{H}_3\times 2$), 1.90, 2.16 (each s, $-CO-CH=C-C\underline{H}_3\times 2$), 2.55 (t, $J=7$ Hz, $-CH_2-$), 5.07 (br t, $J=7$ Hz, $-CH=$), 5.60 (m, $-OCO-CH=$), 5.75 (t, $J=7$ Hz, $-CH-OCO-$), 6.43 (br s, $-OH$), 6.63 (dd, $J=2.5$ Hz, 9 Hz, C_5-H), 6.69 (s, C_8-H), 6.83 (dd, $J=0.8$ Hz, 9 Hz, C_6-H), 6.99 (dd, $J=0.8$ Hz, 2.5 Hz, C_3-H), 7.43 (br s, $C_{10}-H$). PHLC (t_R, min): *ca.* 29.

Shikonofurans D Diacetate (IX) and E Diacetate (X)——Acetylation of a mixture of IV and V (10 mg) in a similar fashion gave a diacetate mixture (5 mg) as a colorless oil. FD-MS *m/z*: 428 (M^+), 440 (M^+). UV λ_{max}^{EtOH} nm: 280. IR $\nu_{max}^{liquid\ film}$ cm^{-1}: 1765, 1730, 1495, 1370, 1205, 1195, 1170, 1030, 915. NMR (in $CDCl_3$) δ: 1.14, 1.16 (each d, $J=7$ Hz, $-CH-C\underline{H}_3\times 2$), 1.62, 1.68 (each s, $=C-CH_3\times 2$), 1.88, 2.16 (each s, $-CO-CH=C-C\underline{H}_3\times 2$), 2.31, 2.36 (each s, $-OCOCH_3$), 2.54 (t, $J=7$ Hz, $-CH_2-$), 5.07 (br t, $J=7$ Hz, $-CH=$), 5.64 (m, $-CO-CH=$), 5.74 (t, $J=7$ Hz, $-CH-OCO-$), 6.68 (br s, C_8-H), 6.96 (dd, $J=2.5$ Hz, 9 Hz, C_5-H), 7.15 (dd, $J=0.8$ Hz, 9 Hz, C_6-H), 7.40 (br s, $C_{10}-H$), 7.49 (dd, $J=0.8$ Hz, 2.5 Hz, C_3-H).

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