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A New Synthesis of 3-Oxosapriparaquinone, a Diterpene from *Salvia prionitis* HANCE (Labiatae)

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5,8,11,13-Abietatetraen-3-one (3) and its 12-methoxy derivative (7) were oxidized to the corresponding 3,7-diones, which were rearranged respectively into 2-isopropyl-6-methyl-5-(4-methyl-3-oxopentyl)naphthalene (6) and its 12-methoxy derivative (10) by sodium borohydride reduction and subsequent dehydration with boron trifluoride etherate. Compound 10 was further converted into 3-oxosapriparaquinone (1) *via* 5-(3-acetoxy-4-methylpentyl)-2-isopropyl-6-methyl-3,4-naphthoquinone (14).

Key words synthesis; 3-oxosapriparaquinone; 4,5-*seco*-abietane diterpene; *Salvia prionitis*

3-Oxosapriparaquinone[1,2] (1) was isolated from the roots of *Salvia prionitis* HANCE (Labiatae), which is used in Chinese folk medicine as an antiphlogistic, antibacterial, and antitubercular drug. This natural diterpene **1** has a rare 4,5-*seco*-abietane structure, possessing a rearranged angular methyl group at the C-5 position.

Recently, we reported on a rearrangement of the angular methyl group in dehydroabietic acid derivatives[3] and the synthesis of 3-oxosapriparaquinone[4] (1). As an extension of the previous work, we further studied the rearrangement of the angular methyl group in dehydroabietic acid derivatives possessing a hydroxyl group at the C-3 position and here describe a new synthesis of 3-oxosapriparaquinone (1). The pivotal step in our present synthesis is a new rearrangement of a dehydroabietic acid derivative into a 3-oxo-4,5-*seco*-abietane derivative.

We first carried out the following preliminary experiment on the rearrangement of the angular methyl group, leading to a 2-isopropyl-6-methylnaphthalene derivative. 5,8,11,13-Abietatetraen-3-one[5] (3) prepared from (+)-dehydroabietic acid (2), was oxidized with Jones reagent in acetone to give a 3,7-dioxo compound (4) in 88% yield. Reduction of **4** with sodium borohydride in the presence of cerium(III) chloride heptahydrate in a mixture of tetrahydrofuran and methanol (1:1) afforded a 3,7-dihydroxy compound (**5**), which, without purification, was treated with boron trifluoride etherate in dichloromethane at room temperature to give the desired 2-isopropyl-6-methyl-5-(4-methyl-3-oxopentyl)naphthalene (**6**) in 82% yield from **4**.

Subsequently, the synthesis of 3-oxosapriparaquinone (**1**) was carried out as follows. As in the case of 3,12-methoxy-5,8,11,13-abietatetraen-3-one[6] (7) prepared from (+)-dehydroabietic acid (**2**) was converted into 2-isopropyl-3-methoxy-6-methyl-5-(4-methyl-3-oxopentyl)naphthalene (**10**, 81% yield from **8**) *via* a 3.7-dioxo compound (**8**, 96% yield) and a 3,7-dihydroxy compound (**9**) by means of a series of reactions: oxidation with Jones reagent, sodium borohydride reduction, and treatment with boron trifluoride etherate. Reduction of **10** with lithium aluminum hydride in ether afforded a hydroxy compound (**11**, 98% yield), which was transformed to the corresponding acetate (**12**, 99% yield) with acetic anhydride in pyridine. To introduce an oxygen function at the C-4 position, compound **12** was demethylated with anhydrous aluminum chloride and ethanethiol in dichloromethane and the resulting naphthol **13** (98% yield) was oxidized with Fremy's salt and potassium dihydrogenphosphate in aqueous *N*,*N*-dimethylformamide to give an orthoquinone (**14**) in 91% yield. The quinone (**14**) was submitted to Thiele–Winter acetoxylation[7,8] with acetic anhydride and concentrated sulfuric acid at 0—5 °C. Since the crude product contained a small amount of phenolic compound, it was further treated with acetic anhydride in pyridine at 85—90 °C to give a tetraacetate (**15**) in 46% yield. Treatment of **15** with lithium aluminum hydride in refluxing tetrahydrofuran gave a dihydroxy-paraquinone (**16**, 88% yield), which was finally oxidized with Jones reagent to give 3-oxosapriparaquinone (**1**) in 81% yield. The synthetic **1** was shown to be identical with natural 3-oxosapriparaquinone by spectral comparisons.

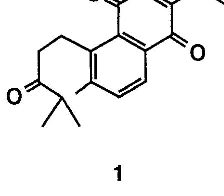

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Fig. 1

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. The IR spectra were measured on a Shimadzu IR-400 spectrometer in chloroform, and the optical rotations were measured with a JASCO DIP-360 polarimeter. The mass spectra were recorded on a JEOL JMS-D300 spectrometer. The ^{1}H-NMR spectra were recorded with a Hitachi R-1500 (60 MHz) or a JEOL JNM EX-400 (400 MHz) spectrometer in deuteriochloroform using tetramethylsilane as an internal standard, and the following abbreviations are used: s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet, br = broad. Column chromatography was performed using Merck silica gel (0.063—0.200 mm).

5,8,11,13-Abietatetraene-3,7-dione (4) Jones reagent (1.0 mol dm^{-3}, 0.65 ml) was added to a stirred solution of 5,8,11,13-abietatetraen-3-one[5]

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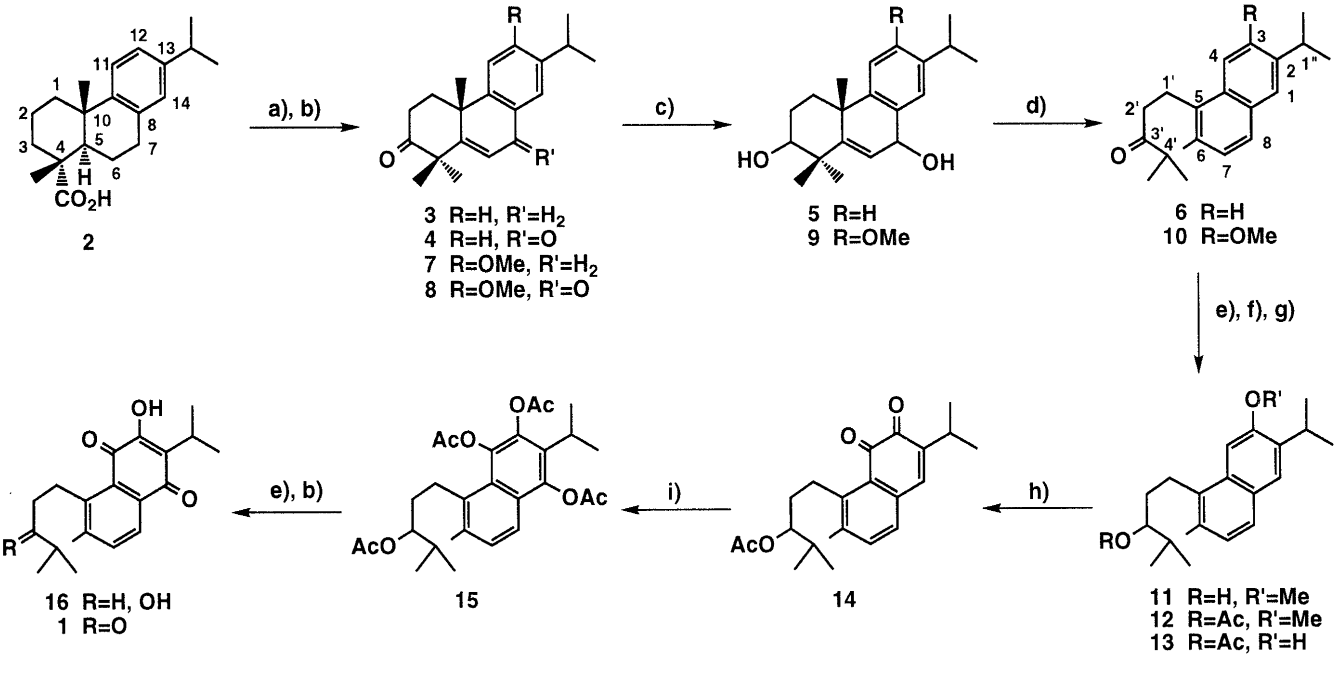

Reagents a) Ref. 5, 6 b) Jones reagent c) $NaBH_4$, $CeCl_3 \cdot 7H_2O$ d) $BF_3 \cdot OEt_2$ e) $LiAlH_4$ f) Ac_2O, pyridine g) $AlCl_3$, EtSH h) Fremy's salt, KH_2PO_4 i) Ac_2O, H_2SO_4 ; Ac_2O, pyridine

Chart 1

(3) (150 mg) in acetone (3.0 ml) with cooling in an ice-water bath. The mixture was stirred at this temperature for 10 min, further stirred at room temperature for 1 h, and then diluted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (20 g), using chloroform as an eluent, to give the starting **3** (34.1 mg). Further elution with chloroform afforded **4** (113 mg, 68% yield; 88% yield based on the starting material consumed). This was recrystallized from acetone–hexane, mp 162—163 °C, $[\alpha]_D$ +96.2° ($CHCl_3$, c=1.41). IR: 1715, 1650 cm^{-1}. ^1H-NMR (60 MHz) δ: 1.30 (6H, d, J=7.3 Hz, $-CH(CH_3)_2$), 1.36, 1.41, 1.48 (each 3H, s, C4-$(CH_3)_2$, C10-CH_3), 6.52 (1H, s, C6-H), 7.47, 7.49 (each 1H, s, C11-H, C12-H), 8.07 (1H, br s, C14-H). HR-MS m/z: Calcd for $C_{20}H_{24}O_2$ (M^+): 296.1776. Found: 296.1775.

Rearrangement of 4 into 2-Isopropyl-6-methyl-5-(4-methyl-3-oxopentyl)naphthalene (6) Sodium borohydride (39 mg) was added to a stirred mixture of **4** (140 mg) and cerium(III) chloride heptahydrate (387 mg) in a mixture of methanol and tetrahydrofuran (1 : 1, 5.0 ml) with cooling in an ice-water bath over a 4-min period. The mixture was further stirred at this temperature for 10 min and then diluted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give a crude diol (**5**, 154 mg). IR: 3600, 3450 cm^{-1}.

A mixture of the above crude **5** (154 mg) and boron trifluoride etherate (0.45 ml) in dichloromethane (4.0 ml) was stirred at room temperature for 1 h. The mixture was diluted with ether, washed successively with dilute hydrochloric acid and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (20 g), using chloroform as an eluent, to give **6** as an oil (109 mg, 82% yield from **4**). IR: 1705 cm^{-1}. ^1H-NMR (400 MHz) δ: 1.11, 1.33 (each 6H, d, J=6.8 Hz, 2-$CH(CH_3)_2$), 2.46 (3H, s, C6-CH_3), 2.59 (1H, m, J=6.8 Hz, C4'-H), 2.73 (2H, t, J=8.3 Hz, C2'-H_2), 3.05 (1H, m, J=6.8 Hz, C1''-H), 3.32 (2H, t, J=8.3 Hz, C1'-H_2), 7.25 (1H, d, J=8.3 Hz, C7-H), 7.40 (1H, dd, J=8.8, 2.0 Hz, C3-H), 7.58 (1H, d, J=8.3 Hz, C8-H), 7.60 (1H, br s, C1-H), 7.88 (1H, d, J=8.8 Hz, C4-H). Differential nuclear Overhauser effects (NOE's) were observed between an isopropyl methyl signal at δ 1.33 and signals at δ 3.05, 7.40, and 7.60, between an aryl methyl signal at δ 2.46 and signals at δ 3.32 and 7.25, and between a methylene signal at δ 3.32 and signals at δ 2.46, 2.73, and 7.88. HR-MS m/z: Calcd for $C_{20}H_{26}O$ (M^+): 282.1984. Found: 282.1979.

12-Methoxy-5,8,11,13-abietatetraene-3,7-dione (8) Jones reagent (2.5 mol dm^{-3}, 4.99 ml) was added to a stirred solution of 12-methoxy-5,8,11,13-abietatetraen-3-one[6] (**7**) (2.082 g) in acetone (21 ml) with cooling in an ice-water bath over a 3-min period. The mixture was stirred at this temperature for 10 min, further stirred at room temperature for 1 h, and then diluted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (150 g), using chloroform as an eluent, to give **8** (2.085 g, 96% yield), which was recrystallized from acetone–hexane, mp 162—163 °C, $[\alpha]_D$ +127.5° ($CHCl_3$, c=0.49). IR: 1715, 1650, 1600 cm^{-1}. ^1H-NMR (60 MHz) δ: 1.25 (6H, d, J=6.9 Hz, $-CH(CH_3)_2$), 1.37, 1.41, 1.47 (each 3H, s, C4-$(CH_3)_2$, C10-CH_3), *ca.* 1.8—2.6 (2H, m, C1-H_2), *ca.* 2.6—3.0 (2H, m, C2-H_2), 3.32 (1H, m, J=6.9 Hz, C15-H), 3.93 (3H, s, C12-OCH_3), 6.48 (1H, s, C6-H), 6.86 (1H, s, C11-H), 8.07 (1H, s, C14-H). HR-MS m/z: Calcd for $C_{21}H_{26}O_3$ (M^+): 326.1882. Found: 326.1862.

Rearrangement of 8 into 2-Isopropyl-3-methoxy-6-methyl-5-(4-methyl-3-oxopentyl)naphthalene (10) Sodium borohydride (177 mg) was added to a stirred mixture of **8** (768 mg) and cerium(III) chloride heptahydrate (1.764 g) in a mixture of methanol and tetrahydrofuran (1 : 1, 20 ml) with cooling in an ice-water bath over a 3-min period. The mixture was further stirred at this temperature for 10 min and then diluted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give a crude diol **9** (845 mg), which was used without purification in the next reaction. IR: 3625, 3450, 3250 cm^{-1}.

A mixture of the above crude **9** (845 mg) and boron trifluoride etherate (3.28 ml) in dichloromethane (20 ml) was stirred at room temperature for 1 h. The mixture was diluted with ether, washed successively with dilute hydrochloric acid and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (100 g), using hexane–chloroform (3 : 7) as an eluent, to give **10** as an oil (598 mg, 81% yield). IR: 1705, 1630, 1605 cm^{-1}. ^1H-NMR (400 MHz) δ: 1.11, 1.30 (each 6H, d, J=6.8 Hz, 2-$CH(CH_3)_2$), 2.45 (3H, s, C6-CH_3), 2.60 (1H, m, J=6.8 Hz, C4'-H), 2.75 (2H, br t, J=8.3 Hz, C2'-H_2), 3.30 (2H, br t, J=8.3 Hz, C1'-H_2), 3.39 (1H, m, J=6.8 Hz, C1''-H), 3.93 (3H, s, C3-OCH_3), 7.13 (1H, d, J=8.0 Hz, C7-H), 7.17 (1H, s, C4-H), 7.53 (1H, d, J=8.0 Hz, C8-H), 7.56 (1H, s, C1-H). Differential NOE's were observed between an isopropyl methyl signal at δ 1.30 and signals at δ 3.39 and 7.56, between an aryl methyl signal at δ 2.45 and signals at δ 3.30 and 7.13, between a methylene signal at δ 3.30 and signals at δ 2.45, 2.75, and 7.17, and between a methoxyl signal at δ 3.93 and a signal at δ 7.17. HR-MS m/z: Calcd for $C_{21}H_{28}O_2$ (M^+): 312.2089. Found: 312.2108.

5-(3-Hydroxy-4-methylpentyl)-2-isopropyl-3-methoxy-6-methylnaphthalene (11) Lithium aluminum hydride (16 mg) was added to a stirred solution of **10** (174 mg) in dry ether (3.0 ml) with cooling in an ice-water bath over a 3-min period. The mixture was stirred at room temperature for 30 min, poured into ice-dilute hydrochloric acid, and extracted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using chloroform as an eluent, to give **11** (171 mg, 98% yield). This was recrystallized from hexane, mp 74—75 °C. IR: 3650, 3490, 3250 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.93 (6H, d, $J=6.5$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 1.30 (6H, d, $J=6.7$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 2.47 (3H, s, C6-CH$_3$), 3.95 (3H, s, C3-OCH$_3$), 7.12 (1H, d, $J=8.5$ Hz, C7-H), 7.34 (1H, s, C4-H), 7.53 (1H, d, $J=8.5$ Hz, C8-H), 7.55 (1H, s, C1-H). HR-MS *m/z*: Calcd for $C_{21}H_{30}O_2$ (M$^+$): 314.2246. Found: 314.2249.

5-(3-Acetoxy-4-methylpentyl)-2-isopropyl-3-methoxy-6-methylnaphthalene (12) A mixture of **11** (905 mg) and acetic anhydride (5.0 ml) in pyridine (5.0 ml) was heated at 75—85 °C for 3 h. After the usual work-up, the crude product was chromatographed on silica gel (20 g), using hexane–chloroform (1 : 1) as an eluent, to give **12** as an oil (1.011 g, 99% yield). IR: 1725, 1635 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.95, 1.30 (each 6H, d, $J=6.7$ Hz, 2-CH(C$\underline{\text{H}}_3$)$_2$), 2.14 (3H, s, C3′-OCOCH$_3$), 2.45 (3H, s, C6-CH$_3$), 3.40 (1H, m, $J=6.7$ Hz, C1″-H), 3.98 (3H, s, C3-OCH$_3$), 4.97 (1H, q, $J=5.9$ Hz, C3′-H), 7.12 (1H, d, $J=8.5$ Hz, C7-H), 7.19 (1H, s, C4-H), 7.51 (1H, d, $J=8.5$ Hz, C8-H), 7.56 (1H, s, C1-H). HR-MS *m/z*: Calcd for $C_{23}H_{32}O_3$ (M$^+$): 356.2351. Found: 356.2355.

5-(3-Acetoxy-4-methylpentyl)-2-isopropyl-6-methyl-3-naphthol (13) Anhydrous aluminum chloride (140 mg) was added to a stirred solution of **12** (33 mg) and ethanethiol (0.1 ml) in dichloromethane (0.5 ml) with cooling in an ice-water bath over a 3-min period. The mixture was stirred at room temperature for 2 h, poured into ice–dilute hydrochloric acid, and extracted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (5 g), using chloroform as an eluent, to give **13** as an oil (31 mg, 98% yield). IR: 3680, 3620, 3350, 1720, 1635 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.94 (6H, d, $J=6.7$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 1.34 (6H, d, $J=7.0$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 1.60—2.15 (3H, m, overlap, C2′-H$_2$ and C4′-H), 2.15 (3H, s, C3′-OCOCH$_3$), 2.43 (3H, s, C6-CH$_3$), 2.71—3.09 (2H, m, overlap, C1′-H$_2$), 3.36 (1H, m, $J=7.0$ Hz, C1″-H), 5.89 (1H, s, C3-OH), 7.09 (1H, d, $J=8.2$ Hz, C7-H), 7.25 (1H, s, C4-H), 7.51 (1H, d, $J=8.2$ Hz, C8-H), 7.57 (1H, s, C1-H). HR-MS *m/z*: Calcd for $C_{22}H_{30}O_3$ (M$^+$): 342.2195. Found: 342.2208.

5-(3-Acetoxy-4-methylpentyl)-2-isopropyl-6-methyl-3,4-naphthoquinone (14) A stirred solution of **13** (55 mg) in *N*,*N*-dimethylformamide (7.0 ml) was protected from light with aluminum foil. After the addition of a solution of Fremy's salt (potassium nitrosodisulfonate, 215 mg) and potassium dihydrogenphosphate (83 mg) in water (8.3 ml), the mixture was stirred at room temperature for 2.5 h under a stream of nitrogen. The mixture was poured into dilute hydrochloric acid and extracted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using chloroform as an eluent, to give **14** as an oil (52 mg, 91% yield). IR: 1720, 1690, 1660, 1630 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.95 (6H, d, $J=6.4$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 1.17 (6H, d, $J=6.7$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 2.13 (3H, s, C3′-OCOCH$_3$), 2.35 (3H, s, C6-CH$_3$), 2.80—3.19 (3H, m, C1′-H$_2$, C1″-H), 4.91 (1H, br q, $J=5.6$ Hz, C3′-H), 7.04 (1H, d, $J=7.9$ Hz, C7-H), 7.09 (1H, s, C1-H). 7.37 (1H, d, $J=7.9$ Hz, C8-H).

1,3,4-Triacetoxy-5-(3-acetoxy-4-methylpentyl)-2-isopropyl-6-methylnaphthalene (15) Concentrated sulfuric acid (0.022 ml) was added to a stirred solution of **14** (60 mg) in acetic anhydride (1.2 ml) with cooling in an ice-water bath. The mixture was stirred at this temperature for 20 min, diluted with water, and extracted with ether. The ether solution was washed with water, dried over sodium sulfate, and evaporated *in vacuo*. The residue was dissolved in acetic anhydride (0.8 ml) and pyridine (0.8 ml), and this solution was heated at 80 °C for 2 h. The mixture was cooled, poured into dilute hydrochloric acid, and extracted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using ether–benzene (1 : 99) as an eluent, to give **15** as an oil (39 mg, 46% yield). IR: 1765, 1725 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.90 (6H, d, $J=6.4$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 1.29 (6H, d, $J=6.7$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 2.12 (3H, s, C3′-OCOCH$_3$), 2.35 (3H, s), 2.45 (9H, br s) (C6-CH$_3$, C1-OCOCH$_3$, C3-OCOCH$_3$, and C4-OCOCH$_3$), 4.80—5.01 (1H, m, C3′-H), 7.25 (1H, d, $J=8.8$ Hz, C7-H), 7.48 (1H, d, $J=8.8$ Hz, C8-H). HR-MS *m/z*: Calcd for $C_{28}H_{36}O_8$ (M$^+$): 500.2410. Found: 500.2424.

3-Hydroxy-5-(3-hydroxy-4-methylpentyl)-2-isopropyl-6-methyl-1,4-naphthoquinone (16) Lithium aluminum hydride (141 mg) was added to a stirred solution of **15** (466 mg) in dry tetrahydrofuran (20 ml) with cooling in an ice-water bath over a 5-min period. The mixture was refluxed for 1 h, poured into ice–dilute hydrochloric acid, and extracted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (20 g), using hexane–chloroform (1 : 1) as an eluent, to give **16** as an oil (272 mg, 88% yield). IR: 3565, 3355, 1645 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 0.96 (6H, d, $J=6.4$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 1.30 (6H, d, $J=7.0$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 2.46 (3H, s, C6-CH$_3$), 3.11—3.62 (4H, m, C1′-H$_2$, C3′-H, C1″-H), 7.52 (1H, d, $J=7.9$ Hz, C7-H), 7.74 (1H, s, C3-OH), 7.99 (1H, d, $J=7.9$ Hz, C8-H). HR-MS *m/z*: Calcd for $C_{20}H_{26}O_4$ (M$^+$): 330.1831. Found: 330.1851.

3-Oxosapriparaquinone (1) Jones reagent (1.0 mol dm^{-3}, 0.3 ml) was added to a stirred solution of **16** (72 mg) in acetone (1.0 ml) with cooling in an ice-water bath. The mixture was stirred at this temperature for 10 min, diluted with ether, and washed with brine. The ether solution was dried over sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on silica gel (20 g), using hexane–chloroform (3 : 7) as an eluent, to give **1** (58 mg, 81% yield), which was recrystallized from hexane to give yellow needles, mp 107.5—108.5 °C. IR: 3370, 1710, 1645 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.16 (6H, d, $J=6.7$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 1.30 (6H, d, $J=7.3$ Hz, –CH(C$\underline{\text{H}}_3$)$_2$), 2.43 (3H, s, C6-CH$_3$), 2.66 (3H, m, C2′-H$_2$, C4′-H), 3.39 (3H, m, C1′-H$_2$, C1″-H), 7.52 (1H, d, $J=7.9$ Hz, C7-H), 7.70 (1H, s, C3-OH), 8.00 (1H, d, $J=7.9$ Hz, C8-H). HR-MS *m/z*: Calcd for $C_{20}H_{24}O_4$ (M$^+$): 328.1675. Found: 328.1678. The synthetic **1** was shown to be identical with natural 3-oxosapriparaquinone (mp 102 °C[1]) by spectral comparisons.

References and Notes

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