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Electrooxidative Functionalizations of Dehydroabietic Acid

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Synopsis. Dehydroabietic acid methyl ester (**1**) was converted into 7-acetoxydehydroabietic acid methyl ester by direct electrooxidation in acetic acid and 7-oxodehydroabietic acid methyl ester by ruthenium dioxide-mediated oxidation. Non-Kolbe type electrodecarboxylation of **1** resulted in the introduction of a double bond into the ring A of **1**.

Dehydroabietic acid[1] (**1a**) is a well-known resin acid of pine tree and usable as a chiral building block for steroid and terpene syntheses.[2] Several oxidative degradations have been attempted to modify the B ring of **1b**,[3] where excess amount of oxidation reagents such as trifluoroperacetic acid, ozone, and hydrogen peroxide have been employed. As one of our research programs on utilization of natural chiral compounds, some of the electrooxidative reactions of **1** have been studied to seek a mild oxidative functionalization of the A and B ring of **1**.

(1) Electro-Acetoxylation on C-7 of 1b. Introduction of acetoxyl group on C-7 of **1b** with cobalt acetate[4] and manganese acetate[5] is unsatisfactory. Meanwhile, electrooxidation of **1b** in an acetic acid–sodium acetate system using carbon electrodes provides **2a** and **2b** in 61 and 13% yields, respectively. The acetate **2a** is a mixture of stereoisomers on C-7 (40:60 by HPLC). To avoid hydrolysis of the acetoxyl group, acetic anhydride was added as a cosolvent, yielding 72% of **2a** along with 3% of **2b**. In contrast to the successful electroacetoxylation using carbon electrodes,[6] the use of platinum electrode was unsuccessful for the present purpose.[7] It is notable that side-chain acetoxylation occurs predominantly on C-7 rather than C-18. A sequence of ECE process, initial one-electron transfer from aromatic ring followed by deprotonation and successive one-electron oxidation leading to a carbenium ion on C-7, would be the most reasonable reaction sequence.[6] Ball-and-stick molecular model reveals that one of the carbon-hydrogen bond orbitals on C-7 overlaps with π-orbital of aromatic ring for the effective deprotonation.

(2) Electrooxidation of Methylene Group on C-7 to Carbonyl Group. Oxidation of methylene group of **1a** and **1b** to carbonyl group has been studied by cobalt acetate-catalyzed oxidation,[3] and chromium trioxide,[8] providing unsatisfactory yield and product-selectivity. Electrooxidation of **1b** in an MeOH-Li-ClO_4-(C) system (20 mA cm^{-2}, 7 F mol^{-1}) gave **3a** and **3b** in 52 and 27%, respectively along with a trace amount of **2c**. On the other hand, electrolysis at a lower current density (1 mA cm^{-2}) gave 7-methoxy compound **2c** (77:23 mixture of stereoisomers) in 79% yield as a sole product. The predominant formation of **3a** and **3b** reveals that **2c** is further oxidized in the high current density to the corresponding dimethyl acetal which would be converted to **3a** by the electrogenerated acid catalysis. No methoxy compound **1c** was detected, suggesting methylene proton on C-7 is much reactive than methine proton of isopropyl group.

Meanwhile, ruthenium tetraoxide-mediated electrooxidation of **1b** was examined in a CCl_4-H_2O-NaCl-HCl-NaH_2PO_4-(Pt) system, using ruthenium dioxide as an oxidant which could be converted to ruthenium tetraoxide by electrooxidatively generated active chlorine species.[9] This method provides **3a** in 52% yield. No hydroxy compound **2b** was detected suggesting the conversion of hydroxyl group to carbonyl group is facile in this system.

(3) Non-Kolbe Type Electrooxidation of 1a. Pb(IV) acetate is one of the most frequently employed oxidative reagents for decarboxylative olefin synthesis.[10] But the yields of **5** and **6a,b** are unsatisfactory. Pyrolysis of **1a** at 450 °C provided a mixture of **5** and **6a,b**.[11] Non-Kolbe type electrooxidation of carboxylic acid is useful for decarboxylative olefin synthesis.[6] Indeed, electrooxidation of **1a** provided a mixture of **5** and **6a,b**, which would arise from the carbenium ion intermediate **4**. The exo-olefin **5** can be transformed into chiral steroidal compounds by Natsumoto's method.[12]

Experimental

Boiling points are indicated by an air bath temperature and uncorrected. The NMR spectra were obtained with JNM FX-100 spectrometer at 100 MHz in $CDCl_3$ using Me_4Si as an internal standard. Acid **1a** was separated and purified from the resin acid mixture according to the reported method,[1] and its methyl ester **1b** was prepared by esterification with diazomethane.

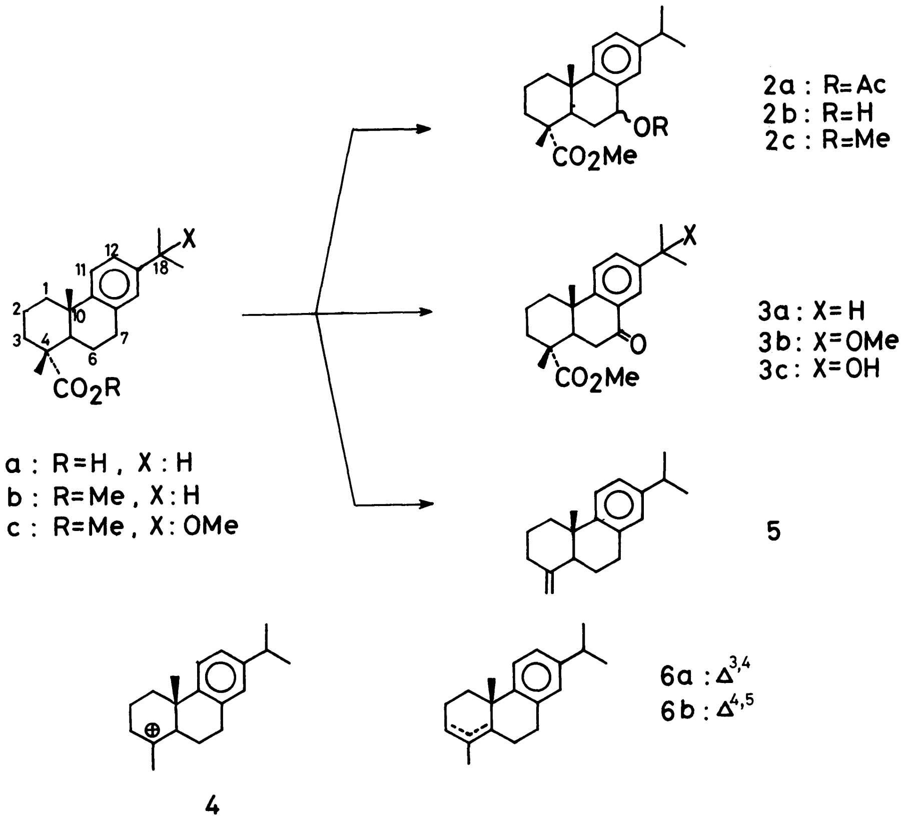
Electrolysis of 1b in Acetic Acid: A mixture of **1b** (100 mg, 0.32 mmol) and AcONa (150 mg, 1.8 mmol) in AcOH (5 ml) and $(Ac)_2O$ (1 ml) was electrolyzed using carbon plate electrodes (3 cm^2) in an undivided cell. After passing 10 F mol^{-1} (1F=96480C, 20 mA cm^{-2}) of electricity, acetic acid was evaporated under reduced pressure and the residue was dissolved in AcOEt. Usual workup and chromatography (SiO_2, hexane-AcOEt=4:1) gave 86 mg (72%) of **3a**, and 3 mg (3%) of **3b**. The structures of **3a** and **3b** were identified by spectroscopic comparison with those of the authentic samples.[5]

Electrolysis of 1b with RuO_2: Two platinum plates (3 cm^2) were settled in a water layer of the reaction mixture which contains **1b** (100 mg, 0.32 mmol) $RuO_2 \cdot 2H_2O$ (22 mg, 0.13 mmol), saturated NaCl containing 0.1 mol dm^{-3}

Table 1. Non-Kolbe Electrooxidation of **1a**

Run	Solv-electrolyte	Yield/%	**5**:**6a**:**6b**[d]
1	MeOH–MeONa	61[a]	58:25:17
2	H_2O–Hexane–KOH	58[b]	55:31:14
3	H_2O–THF–KOH	74[c]	44:38:18

a) 5 mA cm^{-2}, 4 F mol^{-1}. b) 20 mA cm^{-2}, 15 F mol^{-1}. c) 10—1 mA cm^{-2}, 3 F mol^{-1}. d) HPLC analysis.



NaH_2PO_4 (4 ml, pH 4), 10% HCl (0.05 ml), and CCl_4 (2 ml). Constant current (20 $mA\,cm^{-2}$, 30 $F\,mol^{-1}$) was passed at room temperature in an undivided cell. Carbon tetrachloride layer was separated and the water layer was extracted three times with ether. The combined organic extracts were treated as usual, providing **3a**[4] (54 mg, 52%) and **3c**[12] (6 mg, 6%).

Electrolysis of 1b in MeOH: A mixture of **1b** (60 mg, 0.19 mmol), $LiClO_4$ (40 mg, 0.38 mmol), and MeOH (6 ml) was electrolyzed in an undivided cell using two carbon plate electrodes (3 cm^2) [1 $mA\,cm^{-2}$, 14 $F\,mol^{-1}$]. The usual workup gave **2c** (54 mg, 79%). Methyl 1, 2, 3, 4, 4a, 9, 10, 10a-octahydro-9-methoxy-1, 4a-dimethyl-7-(1-methylethyl)-1-phenanthrenecarboxylate (**2c**). Bp 145 °C [4 Torr(1 Torr= 133.322 Pa)]; IR ($CHCl_3$) 2940, 2844, 2801, 1720, 1459, 1242, 1080, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.16 (S, 3H, CH_3), 1.23 (d, J=7 Hz, 6H, CH_3), 1.29 (s, 3H, CH_3), 1.6—2.0 (m, 6H, CH_2), 2.04—3.04 (m, 3H, CH, CH_2), 3.38, 3.41 (S, 3H, CH_3), 3.67 (S, 3H, CH_3), 4.22 (t, J=3 Hz, 1H, $CHOCH_3$ for α-OCH_3 isomer), 4.52 (t, J=8 Hz, 1H, $CHOCH_3$ for β-OCH_3 isomer); Found : C, 76.50; H, 9.56%. Calcd for $C_{22}H_{32}O_3$: C, 76.70 ; H, 9.36 %.

Electrolysis of 1a: A mixture of **1a** (120 mg, 0.4 mmol), 1 mol dm^{-3} KOH (0.4 ml), and THF (6 ml) was electrolyzed in an undivided cell using two carbon plate electrodes (3 cm^2) at a constant terminal voltage (40 V) for 6 hr during which current was dropped from 30 to 3 mA. Silica-gel chromatography of the product gave a mixture of **5**, **6a**, and, **6b**, (76 mg, 74%). Separation of **5**, **6a**, and **6b** was performed by HPLC (μ-porasil, hexane) and the structures were identified spectroscopically.[11,13,14]

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