Table 1. Ga incorporation and sodium ion exchange on mesoporous MCM-41 gallosilcates prepared in this work

Procedure[a]	Si/Ga[b]	Na/Ga[b]	Procedure[a]	Si/Ga[b]	Na/Ga[b]
1	23.66	0.35	2	31.12	0.49
1	44.62	0.61	2	53.34	0.78
1	68.50	0.90	2	84.41	1.01

[a] See the text for the explanation. [b] Atomic ratios determined by inductively coupled plasma emission spectroscopy. A pure-silica sample gave a Na/Si ratio of 0.0005.

was repeated for Ga containing MCM-41 while no remarkable change was observed for pure silica MCM-41 despite of repeated Cu(II) exchange. Such an ion-exchange property indicates gallium incorporation into MCM-41 framework.

To further investigate an ion-exchange properties of Ga-containing MCM-41, calcined producted was ion-exchanged with 10 mM sodium nitrate solution (100 mL per 1g calcined sample) at room temperature with stirring for 2-3 h. To ensure maximum Na^+ ion exchange, This procedure was repeated 3 times. The Na^+ exchanged sample was filtered and washed with deionized water several times to remove external excess Na^+ ions. There were no significant changes in XRD peak intensity before and after Na^+ ion exchange. Elemental analysis for the Si/Ga ratio and Na^+ content was performed with inductively coupled plasma (ICP) emission spectroscopy and the results are summarized in Table 1. The Na^+/Ga ratio increases as the Si/Ga ratio increases. The Na^+ ion exchange was near 100% for the Si/Ga ratios of 70 and higher. Considering that a pure silca MCM-41 gave little ion-exchange, it is evident that Na^+ ion-exchange capacity of the Ga-containing MCM-41 materials comes from Ga incorporation into the MCM-41 framework.

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Oxidation of Pinusolide, *via* an Iodohydrin Intermediate, to 17-Hydroxy-8,13-labdadien-6,15-olid-9-oic Acid Methyl Ester by Treatment with Iodic Acid or Periodic Acid in Aqueous Acetone

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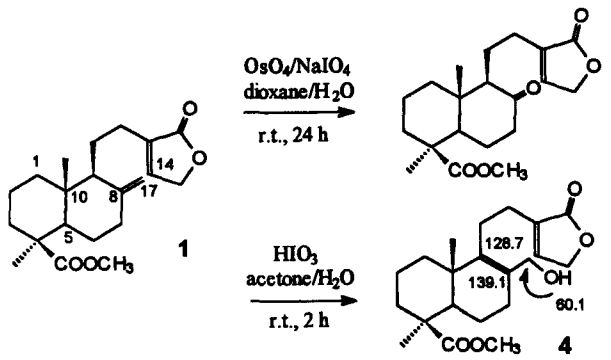
In the course of structure-activity relationship study on pinusolide (8(17),13-labdadien-16,15-olid-19-oic acid methyl ester, **1**), a platelet activating factor antagonist isolated from *Biota orientalis*,[1] we observed that **1** underwent an oxidative transformation to 17-hydroxy-8,13-labdadien-16,15-olid-19-oic acid methyl ester (**4**) on treatment with HIO_3 in aqueous acetone.

Compound (**4**) was first formed as a major product when the reaction condition of oxidation/glycol scission reaction of **1** was changed from $OsO_4/NaIO_4$ (dioxane : H_2O=1 : 1), where **1** was, as expected, oxidized to 17-nor-8-oxo derivative,[2] to OsO_4/H_5IO_6 (acetone : H_2O=5 : 1) in an attempt to increase solubility of **1** in the reaction mixture (Scheme 1). Subsequent studies revealed that **4** was formed in absence of OsO_4 and that use of HIO_3 in place of H_5IO_6 resulted in higher yields.

The structure of **4** was determined by spectroscopic and chemical analyses as 17-hydroxy-8,13-labdadien-16,15-olid-19-oic acid methyl ester. Its molecular weight was 362, 16 mass unit greater than that of **1**. In ^1H NMR, two singlet peaks at 4.56 and 4.87 ppm due to the exocyclic methylene protons in **1** were substituted by two oxymethylene doublet peaks at δ 4.11 and 4.24 ppm in **4**. When **4** was subjected to acetylation with acetic anhydride and pyridine, acetyl pro-



Scheme 1. Oxidative transformation of **1** under different reaction conditions.

tons were observed at δ 2.1 ppm and the oxymethylene proton peaks were shifted to δ 4.50 and 4.64 ppm, indicating the presence of a hydroxyl group in **4**. In ^{13}C NMR spectra of **4**, peaks at δ 139.1 (C-8, quart by DEPT), 128.7 (C-9, quart) and 60.1 (C-17, -CH_2-) ppm were observed instead of the peaks at δ 147.1 (C-8, quart), 55.7 (C-9, -CH<) and 106.7 (C-17, =CH_2) in **1**. Taken together, the structure of **4** was assigned to contain an exocyclic -CH_2OH group with the double bond between C-8 and C-9. The structure of **4** was further confirmed by the fact that upon oxidation with pyridinium dichromate in CH_2Cl_2, the -CH_2OH group in **4** was converted to an aldehyde group (^1H NMR, δ 10.14 (1H, s); ^{13}C NMR, δ 189.8 (C-17)).

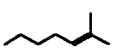
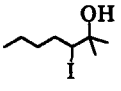
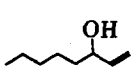
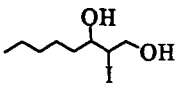
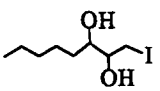
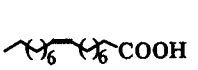
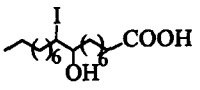
In order to shed light on the mechanism, simple and functionalized olefins were treated with HIO_3 (2 equiv) in aqueous acetone under identical conditions. All the olefins examined were converted to corresponding iodohydrins in high yields (Table 1). The structure of iodohydrin was determined by means of ^1H NMR and mass spectroscopic data, and the orientation of addition reaction was determined by using mass fragmentation data. Diagnostic ^1H NMR and mass data are presented in Table 1.

These results suggested that hypoiodous acid, HOI, is generated in the reaction mixture and that acetone seemingly functions as a reducing agent to generate HOI, an active species, from HIO_3 or H_5IO_6. Among other organic solvents investigated, only methyl ethyl ketone, but neither dioxane, DMF, methanol, ethyl acetate, nor $CHCl_3$ was able to substitute acetone in the reaction. This was taken to indicate the participation of the enol form of acetone. Similar related reactions have been reported in literature, where dicyclopentadiene and dihydroxyacetone were indicated to reduce H_5IO_6 to HOI and HIO_3, respectively.[3]

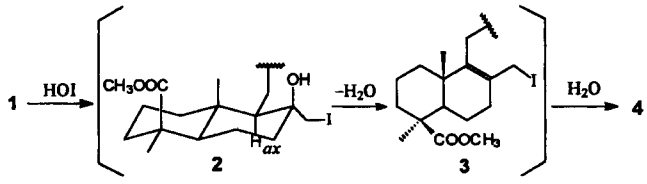
It should be noted that the orientation of the reaction for trisubstituted olefin (run 1 in Table 1) obeyed Markovnikov rule, where iodine was bonded to the less substituted carbon. On the other hand, the reaction with 1-octen-3-ol (run 2) obeyed anti-Markovnikov rule producing 2-iodo-octan-1,3-diol as a major product (77%). This is in accordance with the literature, where $H_5IO_6/NaHSO_3$ in aqueous CH_3CN was employed and electrostatic repulsion of the attacking water molecule by the neighboring hydroxyl group was proposed for the reason for the anti-Markovnikov addition.[4] Interestingly, the reaction with oleic acid (run 3) proceeded fairly regioselectively, producing 9-hydroxy-10-iodo-octadecanoic acid as a major product (80%).

On the basis of these results, the reaction pathway for the conversion of **1** to **4** could be proposed as shown in Scheme 2. It involves an attack of iodonium ion (I^+) donated by HOI to the C-(8-17) double bond from the less hindered α-face, followed by an addition of water (or OH^-) from the opposite side (*anti* addition). This should produce an iodohydrin intermediate, **2**, where iodine is bonded to the terminal carbon (C-17), as the reaction would obey Markovnikov rule. Subsequent *anti* elimination of a water molecule from the axial -OH at C-8 with the axial proton at

Table 1. Conversion of olefin to iodohydrin by HIO_3 in aqueous acetone and diagnostic ^1H NMR and mass data of iodohydrin

Run	Substrate	Product (yield,[a] %)	^1H NMR δ (ppm)	Mass (m/z, %)
1		 (69)	4.11 (1H, m, -CH(I)-)	[M^+], 256 (1.30) [a^+], 129 (88.1) **[b^+], 59 (100)** [a^+-H_2O], 111 (28.1)
2		 (77)	**2.11 (1H, d, *J*=7.5 Hz, -CH(OH)-)** **2.50 (1H, m, -CH_2(OH))** 3.06 (1H, m, -CH(I)-) 3.83, 3.99 (each 1H, m, -CH_2OH) 4.27 (1H, m, -CH(OH)-)	[M^+], 272 (1.25) **[· $CHICH_2^+$], 154 (100)** [a^+], 145 (39.3) **[b^+], 101 (9.73)** [a^+-$2H_2O$], 109 (63.2)
		 (7.4)	**2.01, 2.36 (each 1H, d, *J*=4.8 Hz, -OH)** 3.41 (2H, m, -CH_2(I)-) 54, 3.67 (each 1H, m, -CH(OH)-)	[M^+], 272 (12.2) [M^+-OH], 255 (63.1) [a^+], 145 (29.8) [a^+-$2H_2O$], 109 (100)
3		 (80)	2.89 (1H, m, -CH(I)-) 4.19 (1H, m, -CH(OH)-)	[M^+], 440 (0.03)[b] [a^+], 313 (19.1) **[b^+], 187 (16.4)** [a^+-CH_3OH], 281 (100)

[a] Isolation yields. [b] Mass data was obtained after the product was methylated with CH_2N_2. The most diagnostic data are in bold face.



Scheme 2. Conversion of pinusolide (**1**) *via* iodohydrin intermediate (**2**) to 17-hydroxy-8,13-labdadien-16,15-olid-19-oic acid methyl ester (**4**) by treatment with HIO_3 in aqueous acetone.

C-9 (Zaitsev elimination) should yield an allylic iodo intermediate, **3**, which is then readily hydrolyzed to give **4**.[5] The observation that **1** was successfully converted to **4** by the known procedures of iodohydrin formation from olefin, I_2/H_2O[6] and $HIO_3/NaHSO_3$[4] provided a strong support for the proposed reaction pathway shown in Scheme 2. Therefore, treatment with HIO_3 in aqueous acetone provides an efficient alternative method for preparation of iodohydrin from olefin using easily accessible reagents.

Experimental

Melting point was measured on a Mitamura Riken heat block and uncorrected. ^1H NMR and ^{13}CMR spectra were recorded on a Varian Gemini 2000 spectrometer with chemical shifts expressed in δ (ppm) values. IR spectrum was recorded on a Jasco FT/IR-5300 spectrophotometer (KBr pellet). EI mass (EIMS) and high resolution mass (HREIMS) spectra were run on VG TRIO-II GC/MS and HP 5890-JMS AX 505 WA GC-MASS spectrometer, respectively.

17-Hydroxy-8,13-labdadien-16,15-olid-19-oic acid methyl ester (4). To a stirred solution of **1** (3 g, 8.6 mmol) in 80 mL acetone was slowly added HIO_3 (1.52 g, 8.6 mmol) dissolved in 20 mL H_2O at room temperature. The reaction mixture was allowed to react for 2 h, and treated with 150 mL of H_2O. The ether extract was washed with brine and dried over Na_2SO_4. Following evaporation, the organic extract was subjected to silica gel column chromatography ($CHCl_3$: MeOH=100 : 1, R_f=0.2) *to give pure* **4** in white crystals (2.5 g, 80%): mp 134-6 °C (uncorr.); HREIMS [m/z 362.2090; Δ −0.3 mmu $(M)^+$]; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.84 (s, -CH_3), 1.25 (s, -CH_3), 3.67 (s, -OCH_3), 4.11 (1H, d, *J*=11 Hz, -CH_2OH), 4.24 (1H, d, *J*=11 Hz, -CH_2OH), 4.83 (2H, dd, *J*=2.1, 0.8 Hz, lactonyl=$CHCH_2O$-), 7.19 (1H, t, *J*=0.8 Hz, lactonyl =$CHCH_2O$-); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.6, 16.2, 17.2, 22.4, 24.6, 25.2, 26.6, 33.6, 34.4, 36.5, 40.7, 48.0, 50.0, 60.1, 67.1, 128.7, 131.2, 139.1, 141.2, 171.4, 175.0; IR (KBr) 1694 (lactone, intramolecular hydrogen-bonded), 1761 (ester, C=O), 3542 (sharp, intramolecular hydrogen-bonded allylic OH); GC-MS (EI, m/z, 70 eV, rel. int. %) 362 (M^+, 6.0), 344 (M^+-H_2O, 1.5), 173 (100); Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.59; H, 8.34. Found: C, 69.57; H, 8.42.

General method of conversion of olefins to iodohydrins. In a typical reaction, an olefin (0.3 g) dissolved in 5 mL acetone was added to HIO_3 (2 equiv) solution in water (1 mL). After the mixture was stirred for 12 h at room temperature to complete the reaction, a workup sequence of ether extraction and silica column chromatography afforded the corresponding iodohydrin.

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A New NMR Chiral Solvating Agent Derived from (R)-4-Hydroxyphenylglycine

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Recently we reported the preparation and application of a new chiral stationary phase (CSP **1**) derived from (R)-4-hydroxyphenylglycine for the liquid chromatographic separation of enantiomers.[1] CSP **1** was found to be very excellent in separating the two enantiomers of racemic N-(3,5-dinitrobenzoyl)-α-amino acid amides and esters. The high enantioselectivity of CSP **1** for the two enantiomers of racemic N-(3,5-dinitrobenzoyl)-α-amino acid amides and esters prompted us to extend the use of the chiral selector of CSP **1** as a chiral solvating agent (CSA) for NMR spec-