Figure 1. (A) ¹H-NMR spectrum of imino and aromatic region of echinomycin-[d(CGTACG)]₂ 2:1 complex, in 0.4 m*l* of 0.1 M NaCl, 10 mM phosphate, pH 7 buffer, at 1℃. Spectrum was acquired by using the jump and return pulse sequence[5] $(90°_x - \Delta-90°_{-x})$ to suppress the water resonance. $\Delta = 80$ μsec was used. This sample was used for the NOE of Figure 1B. (B) NOE difference spectrum was obtained with preirradiation of central A · T imino proton resonance for 300 msec. (C) NOE difference spectrum of echinomycin complex with DNA deuterated at the adenosine H-8 position; otherwise similar to (B). Dashed lines connect resonance position of adenosine H-8 proton

NOE experiments were perfomed by selectives saturation of A · T imino proton resonance. We were unable to observe NOE at room temperature because of rapid exchange of this imino proton with the water.[2] At 1℃, however, strong intrabasepair NOE was observed between T imino and AH8 proton resonances (Figure 1B). In the same experiment with [d(CGTA(D)CG)]₂-drug complex, no NOE was detected(Figure 1C). If the central A · T base pair is a standard Watson-Crick A · T base pair which has an adenosine H-2 proton adjacent to the imino proton, the NOE should remain intact in a sample of H-8 deuterated DNA-drug complex. Therefore these data clearly confirm that the observed NOE in Figure 1B originates from the short T imino-AH8 distance which is expected for Hoogsteen A · T base pairing.

In conculsion, we have demonstrated a strategy of unusual base pair identification combining NOE with specific deuteration. The method should be applicable to other unusual DNAs as well as RNAs.

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Photoacoustic Detection of C₆₀

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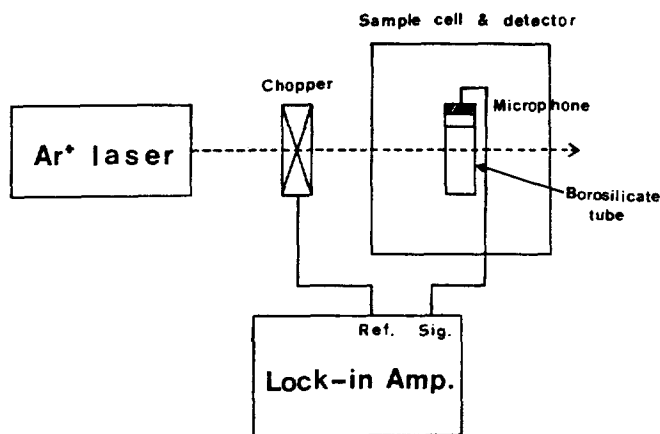*Department of Chemistry, Jeonbuk National University, Jeonju 560-756*
*Department of Chemistry, Seonam University, Namwon 590-170
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Since the discovery of a carbon compound with a molecular weight of 720 by Smalley in 1985, a new form of solid carbon allotropes, C₆₀ has been intensively studied to identify its physical properties and chemical reactivities.[1-4] The unique geometry, known as an icosahedral structure, and the possession of superconductivity[5] of this compound have stimulated a strong interest in wide research areas. Many spectroscopic properties for the Bucknimsterfulleren have been already reported in a short time through the experimental investigations such as IR,[2] UV-visible,[2] MASS,[6] NMR,[6] Raman,[7] and ESR,[8] etc.. In addition, the energy level and the thermodynamic data have been obtained by the theoretical calculations.[9,10] In spite of such booming works, there has been little progress in the study of reactions with C₆₀ due to its aromaticity which might inhibit the chemical reaction. Recently, several reports[12-17] on the reactions of C₆₀ have opened the possibilities of further investigations regarding the reactions with the compound in many aspects of chemistry. In order to study the chemical reactions, in general, it is essential to monitor the concentration of the species participated in the reaction giving rise to the need of a simple and accurate detection for quantitative analysis. In this communication, we utilized a relatively simple photoacoustic method to detect a low level of C₆₀ in the solution.

A block diagram of photoacoustic (PA) system used in this study is shown in Figure 1. The output beam of an argon ion laser (Coherent, Innova 300), operating at 351 nm, was modulated at a frequency of 29 Hz by light chopper (EG&G-9417) and was directed into the sample cell. The sample cell was made of a Borosilicate glass tube with a volume of 2 m*l*. An electret microphone with a built-in FET preamplifier was placed at the end of the acoustic tube. The pressure changes due to the radiation through the sample solution were detected by the microphone and amplified by a lock-in amplifier (EG&G PARC, 5210) with the time constant

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Sample cell & detector

Chopper

Ar⁺ laser

Microphone

Borosilicate tube

Ref. Sig.

Lock-in Amp.

Figure 1. Schematic diagram of experimental setup for the photoacoustic detection of C_{60}.

Concentration in logarithmic scale
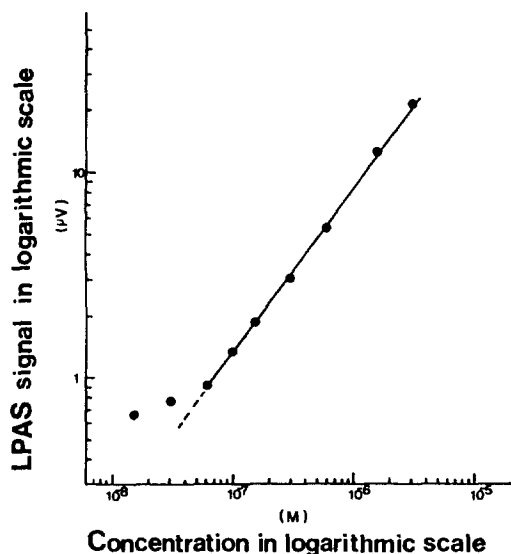
Figure 2. Photoacoustic signal dependene of concentration of C_{60}.

set to 300 msec. The C_{60} in this work was prepared according to the recipe of Huffman *et al.*[4] and characterized by the UV-visible, IR, ^{13}C-NMR, and MASS. A stock solution of fullerene was prepared by dissolving 720 µg of C_{60} in 100 m*l* of benzene to give the concentration of 10^{-5} M.[19] Sample solutions were made by the appropriate dilution of the stock solution of C_{60}. As a solvent, a spectral grade of benzene was used without further purification.

In dilute solution, the intensity of PA signal is proportional to the incident intensity of radiation and the concentration of solute. Consequently, in a given solvent with fixed laser power, the PA signal has shown to possess the linear dependence on the concentration of C_{60} as demonstrated in Figure 2. In this figure, it is also observed that the detection linearity is lost due to the dominant background noise including the solvent absorption and system noises below the concentration of 40 ng/m*l*. The detection limit of C_{60} is determined to be 20 ng/m*l* (20 ppb, 3×10^{-8} M) where the signal-to-noise ratio (S/N) is approximately 2 to 1. The photoacoustic signals are affected by physical conditions of the experiment such

as the wavelength and power of light source used, chopping frequency, and the physical properties of solvent and solute. Since, for the microphone detection technique in solutions, low modulated frequency is preferred due to the thermal diffusion length in the sample,[20] the experiments were carried out at the frequency of 29 Hz. The C_{60} has known to show a broad absorption bands ranging from 211 nm to 635 nm with a large extinction coefficient at the wavelength of 330 nm in benzene solution.[21] Because of the nearest obtainable wavelength in this region with an Ar ion laser, the experiment was performed at 351 nm.

Note that our experimental setup did not achieve the optimum condition for the detection of ultra trace quantities of liquid sample. However the value preliminarily reported here was found to be better at least by a order of magnitude than that from the separate experiment with a conventional UV spectrophotometer. Several changes in the design of the detection method described in this communication can be made to improve the observed detection limit. First, since the wavelength used in the experiment was not optimized at the region of the maximum extinction coefficient of C_{60}, different light sources, such as a easily available ultraviolet lasers (*e.g.*, excimer laser or N_2 laser) set for a larger molar absorption coefficient, could be expected to yield an even higher detection sensitivity. Secondly, introducing a pulsed laser in conjuction with a PZT and gated electronics can provide a means to allow much higher detectability of the sample.

Conclusively, based on the ideas and data described above, the photoacoustic detection technique has been demonstrated as a simple, rapid, and direct detection mean for C_{60}. With a sufficiently low enough value for the detection presented here, it can be used for a number of applications in the C_{60} chemistry; as an example, to monitor the concentration of the sample for a kinetic study of C_{60} dissolved in solvents.

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19. Because of its relatively high dissolving power for C$_{60}$, benzene has been widely used as a solvent in preperation, separation and chemical reaction of C$_{60}$.

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Synthesis of Optically Active O-Protected 2,3-Dihydroxy Aldehyde

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Optically active 2,3-diol units are widely distributed in the biologically active natural products such as macrolides and polyether antibiotics, etc. Recently, synthesis of syn-2,3-diol esters by asymmetric oxidation reactions of olefin esters using osmium tetroxide with a chiral ligand has been developed.[1] Also, synthesis of anti-2,3-diol esters by asymmetric aldol reaction between aldehydes and silyl enol ethers derived from α-benzyloxy thioesters with a chiral ligand was reported.[2] There still remains a need for the synthesis of optically active syn- and anti-diols on practical point of view. In connection with our current programs on the asymmetric synthesis of optically active natural products from D-glucose
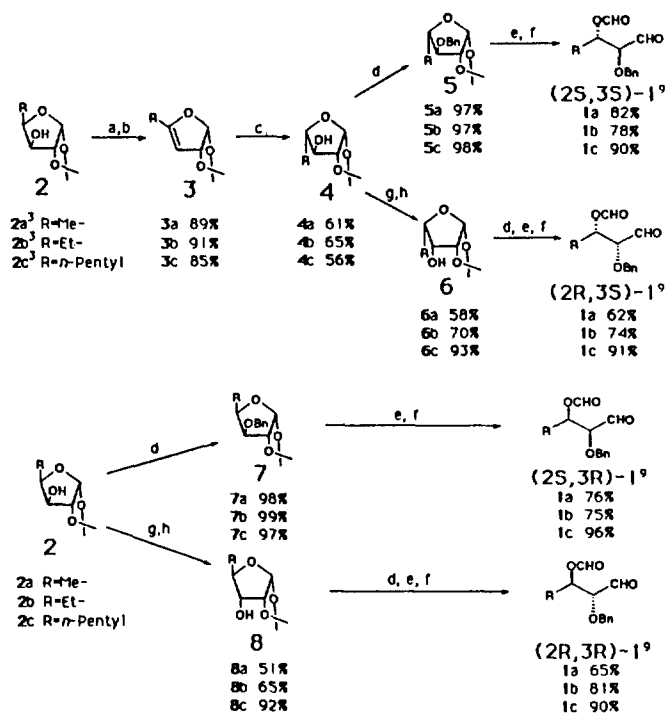
(a) Tf$_2$O, Pyr, CH$_2$Cl$_2$, −10°C (b) DBU, ether, rt (c) Sia$_2$BH, THF, 0°C →rt (d) NaH, BnCl, THF, rt (e) 2 N HCl, DME, rt (f) NaIO$_4$, MeOH, rt (g) DMSO, (COCl)$_2$, Et$_3$N, CH$_2$Cl$_2$, −60°C →rt (h) NaBH$_4$, MeOH, −78°C.

Scheme 1

or D-xylose, we needed the appropriately protected syn- and anti-2,3-dihydroxy aldehydes 1. Here we report a stereocontrolled synthesis of optically active four stereoisomers of 2,3-dihydroxy aldehydes by chemical modification of the α-D-glucofuranose or α-D-xylofuranose, which in turn were prepared from D-glucose or D-xylose.

Hex-3-enofuranose 3a-c were prepared[3] by the elimination reaction of the triflates derived from C-3 hydroxyfuranoses 2a-c.[4,5] Hydroboration of 3b with disiamylborane followed by oxidation with H$_2$O$_2$/NaOH afforded 3-hydroxyl-β-L-threo-hexofuranose 4b[6] (TLC : SiO$_2$, EtOAc/Hexanes=1 : 1, R_f= 0.48), [α]$_D^{25}$ −25.5° (*c* 0.44, CHCl$_3$) exclusively as the only isolated produce[7] in 65% yield after column chromatographic separation. Orientation of the ethyl- and hydroxy- substituents of 4b and excellent stereoselectivity (>99%)[7] were confirmed by the comparison of the ¹H- and ¹³C-NMR spectra and capillary GLC data of 4b and 8b (Scheme 1).[8] Surprisingly, by capillary GLC analysis, only one isomer was detected before and after column chromatographic separation. Even if hydroboration of 3b with BH$_3$·SMe$_2$ followed by oxidation with H$_2$O$_2$/NaOH also gave 4b as a major product by checking GLC, hydroboration of 3b with disiamylborane followed by oxidation afforded 4b as the only isolated product without any impurities. Removal of the isopropylidene group in 5b with 2 N HCl provided the hemiacetal, which was subjected to oxidative cleavage with sodium periodate to afford the (2S, 3S)-2-benzyloxy-3-formyloxy-1-pentanal 1b[9] (TLC : SiO$_2$, EtOAc/Hexanes=1 : 1, R_f=0.62), [α]$_D^{25}$ −61.8° (*c* 0.60, CHCl$_3$) (Scheme 1). The reaction sequence was also applied to prepare (2S, 3S)-1a and (2S, 3S)-1c,