which is shown in Scheme 1.[8] The C-3 β-hydroxy-group in **4b** was converted to α-hydroxy-group. Swern oxidation of **4b** followed by reduction with $NaBH_4$ in MeOH at −78℃ afforded **6b**[6] as the only isolated product by checking GLC data of **6b** and **4b**. The compound **6b** was converted to the (2*R*, 3*S*)-2-benzyloxy-3-formyloxy-1-pentanal **1b**[9] (TLC : SiO_2, EtOAc/Hexanes = 1 : 1, R_f = 0.62), $[\alpha]_D^{25}$ +46.3° (*c* 1.0, $CHCl_3$) (Scheme 1). The reaction sequence was also applied to prepare (2*R*, 3*S*)-**1a** and (2*R*, 3*S*)-**1c**, which is shown in Scheme 1.[8]

Alternatively, (2*S*, 3*R*)- and (2*R*, 3*R*)-2-benzyloxy-3-formyloxy-1-alkanals were easily prepared from **2**. Benzylation of **2b**[6] gave the benzyloxy compounds **7b**, which was converted to the (2*S*, 3*R*)-2-benzyloxy-3-formyloxy-1-pentanal **1b**,[9] (TLC : SiO_2, EtOAc/Hexanes = 1 : 1, R_f = 0.62), $[\alpha]_D^{25}$ −47.0° (*c* 0.2, $CHCl_3$) (Scheme 1). The reaction sequence was also applied to prepare (2*S*, 3*R*)-**1a** and (2*S*, 3*R*)-**1c**, which is shown in Scheme 1.[8] On the other hands, Swern oxidation of **2b** followed by reduction with $NaBH_4$ in MeOH at −78℃ afforded **8b**.[6] The compound **8b** was converted to the (2*R*, 3*R*)-2-benzyloxy-3-formyloxy-1-pentanal **1b**[9] (TLC : SiO_2, EtOAc/Hexanes = 1 : 1, R_f = 0.62), $[\alpha]_D^{25}$ + 51.3° (*c* 1.97, $CHCl_3$) (Scheme 1). The reaction sequence was also applied to prepare (2*R*, 3*R*)-**1a** and (2*R*, 3*R*)-**1c**, which is shown in Scheme 1.[8]

We have used optically active *O*-protected 2,3-dihydroxy aldehydes prepared by this methodology in the enantioselective syntheses of L-factor and muricatacin.[10]

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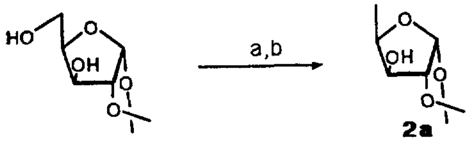
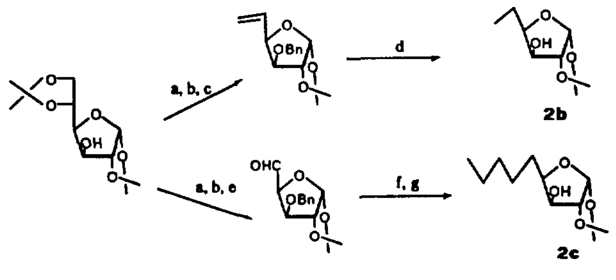
4. The compound **2a** was prepared from 1,2-*O*-isopropylidene-D-xylofuranose in two steps; (a) *p*-TsCl, pyridine, $CHCl_3$, 0℃, 12 h (79%); (b) $LiAlH_4$, THF, reflux, 12 h (96%).



5. The compounds **2b** and **2c** were prepared conventionally from diacetone-D-glucose by the following reaction sequence (a) NaH, $PhCH_2Cl$, THF, rt, 24 h (98%); (b) 50% HOAc, rt, 24 h (96%); (c) *N,N*-dimethylformamide dimethylacetal, rt, 1 h and then Ac_2O, 160℃, 3 h (71%); (d) H_2, EtOAc, Pd/C (97%); (e) $NaIO_4$, CH_2Cl_2, rt, 1 h (99%); (f) $(C_6H_5)_3P=CHCH_2CH_2CH_3$; (g) H_2, Pd/C, EtOAc, rt, atmospheric pressure, 24 h (88%).



6. $[\alpha]_D$ values at 25℃ (concentration in $CHCl_3$).

2a:	−18.4°(2.93)	**4a**:	−12.7°(3.0)	**6a**:	+14.2°(2.1)	**8a**:	+41.0°(1.0)
2b:	−8.0°(2.0)	**4b**:	−25.5°(0.44)	**6a**:	+54.2°(0.28)	**8b**:	+61.7°(1.45)
2c:	−18.0°(1.0)	**4c**:	−16.7°(1.73)	**6c**:	−61.1°(0.10)	**8c**:	−95.3°(0.15)

7. Capillary GC analyses were performed for **2a-c**, **4a-c**, **6a-c**, **8a-c** using Hewlett-Packard 5880 GC system (column: Supelcowax 10, 0.25 mm×30 m, oven temp: **a**: 140℃, **b-c**: 120℃→200℃, carrier gas: N_2, 1.0 m*l*/min, injection temp: 250℃). The values of the retention time for each compounds were as follows: **2a**: 19.36 min, **2b**: 16.30 min, **2c**: 23.21 min, **4a**: 27.51 min, **4b**: 18.49 min, **4c**: 25.87 min, **6a**: 7.85 min, **6b**: 9.58 min, **6c**: 16.64 min, **8a**: 6.72 min, **8b**: 8.81 min, **8c**: 15.57 min.
8. All new compounds gave spectral data (IR, ^1H and ^{13}C-NMR) in accord with the assigned structure.

9. $[\alpha]_D$ values at 25℃ (concentration in $CHCl_3$).

	(2*S*, 3*S*)-1	(2*R*, 3*R*)-1	(2*R*, 3*S*)-1	(2*R*, 3*S*)-1
1a	−58.0°	+50.3°	+24.6°	−28.9°
	(0.90)	(0.3)	(0.56)	(0.98)
1b	−61.8°	+51.3°	+46.3°	−47.0°
	(0.60)	(1.97)	(1.0)	(0.21)
1c	−44.1°	+43.1°	−25.9°	+15.8°
	(0.50)	(1.50)	(1.42)	(0.50)

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Atomic Emission Detector for Gas Chromatography using Cylindrical Microwave Cavity

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The microwave induced plasma (MIP) has been increasingly applied as an excitation source for the emission detector of gas chromatography (GC).[1-5] The MIP detector is known to have high sensitivity and element selectivity, be-

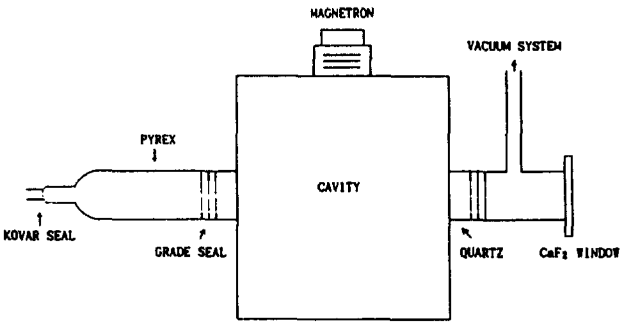

Figure 1. Schematic diagram for cylindrical cavity and plasma tube.

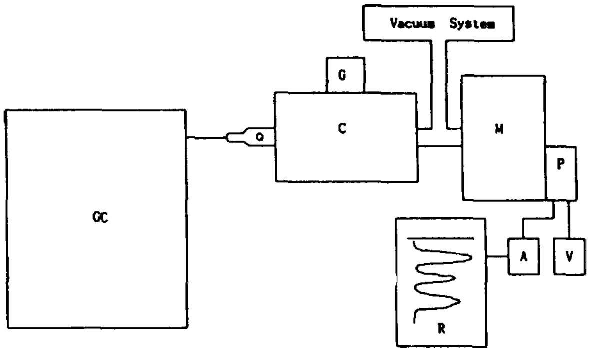

Figure 2. Schematic diagram of MIP/GC system: (GC) Gas Chromatograph, HP5890A; (C) Cavity; (Q) Quartz Tube; (G) Magnetron; (M) Monochromator; (P) PM tube; (A) Picoammeter, Keithley 485; (V) Power Supply; (R) Recorder.

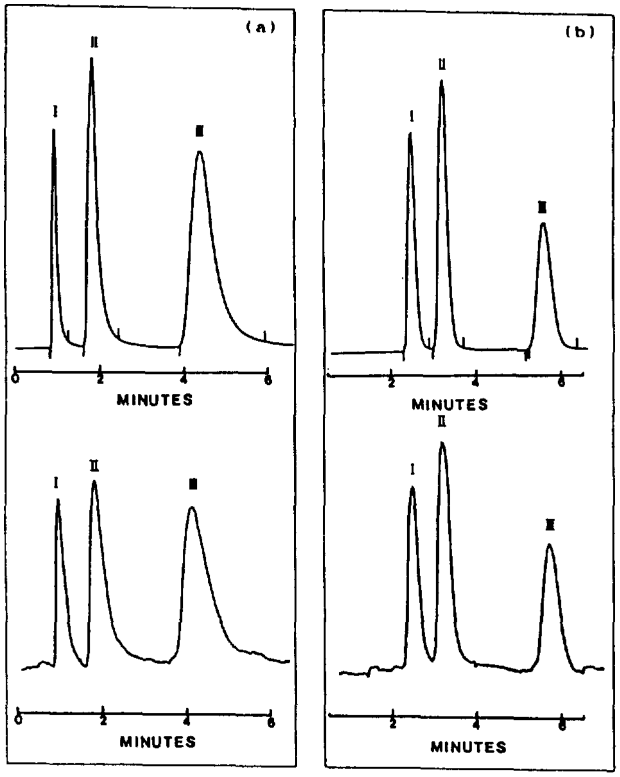

Figure 3. Chromatograms by FID (upper part, recorded by integrator HP 3390A) and MIP detector (bottom part, recorded by strip chart recorder Houston instrument, D5117-5AQ): (a) Alcohols, CH_3OH (I), C_2H_5OH (II), and C_3H_7OH (III); (b) Methyl Chlorides, CCl_4 (I), CH_2Cl_2 (II), and $CHCl_3$ (III).

Table 1. Sensitivity and Detection Limit of MIP Detector for Alcohols and Methyl Chlorides

Compound	Wavelength (nm)	Sensitivity (C/g)[a]		Detection Limit (ng/s)	
		Compound	Element	Compound	Element
CH_3OH	486.1	1.49	11.9	0.21	0.026
C_2H_5OH	486.1	2.15	19.8	0.14	0.018
C_3H_7OH	486.1	6.34	47.6	0.052	0.007
CH_2Cl_2	479.5	0.05	0.06	4.6	3.83
$CHCl_3$	479.5	0.041	0.046	6.26	5.65
CCl_4	479.5	0.038	0.042	6.14	5.66

[a] PMT cathode voltage was at −800 V.

cause the selected atomic emission line is used for monitoring. The MIP detector has advantages for the determination of eluted components over the electron capture or the flame ionization detectors, which respond to the given classes of compounds.[4,5] After the first type of MIP/GC detector was introduced by McCormack *et al.*,[6] several types of microwave cavity have been proposed for the plasma generation.[7,8] Among these types of cavities, Beenakker cavity has been frequently employed since it can work under atmospheric pressure.

In this paper we describe an inexpensive cylindrical cavity system as an MIP/GC detector originally proposed by Meiners and Alford.[9] Major components of this system are a cylindrical cavity and a magnetron. The magnetron (Samsung 2M 209A, 2.45 GHz) is a part of home microwave oven readily available in the market. The cavity, 21 cm in diameter and 19 cm in length, was constructed with 2 mm thick brass plate. The magnetron was mounted directly to the cavity wall and the operating voltage was properly adjusted with a variable autotransformer.[9] One side of 14 mm outer diameter quartz tube was connected to GC column outlet by grade seal, Kovar seal, and 1/16" stainless steel tubing. As shown in Figure 1, the CaF_2 window was attached to the other side of the tube to transmit emission lines through. The vacuum system was connected to the tube and the pressure inside was controlled to stabilize the plasma. The schematic diagram of GC/MIP system is shown in Figure 2. The emission line of the MIP system was observed by Spex 1681 monochromator (0.22 m) equipped with R580 (Hamamatsu) photomultiplier tube and a picoammeter.

A Porapak Q (80/10 mesh) packed stainless steel column was employed for mixtures of alcohols and a 10% Carbowax 20 M on Chromosorb WHP (100/120 mesh) column for methyl chlorides. The flow rate of helium carrier gas was maintained at 20 ml/min. The sample mixture was prepared to contain 0.1 volume % of each component in *n*-hexane. The injector temperature was 150℃ and 0.1 μl sample was injected. The chromatograms shown in the bottom part of Figure 3 were obtained by monitoring H 486.1 nm emission line for alcohols and Cl 479.5 nm emission line for methyl chlorides.[10] The chromatograms by MIP detector are compared to those of flame ionization detector (FID, upper part of Figure 3). Table 1 summarizes sensitivities and detection limits of compounds and elements observed. For alcohols, detection limit varies in the range of 26 pg/s to 7 pg/s upon increasing carbon number of compounds. In contrast, methyl chlorides gave around 5 ng/s of detection limit for chlorine and the values are not different significantly with the number of chlorines in the molecules. The sensitivity and detection limit of this system are comparable to those of FID for alcohols at this moment. Further, this system can be applied for selective monitoring of chlorine-containing molecules. Therefore with this system, it is possible to analyze unresolved peak which could not be separated completely in a typical GC column. Moreover, the MIP detector is sensitive for not only hydrogen or chlorine, but also most elements in principle, so this system has potential prospect for FID-inactive molecules, *e.g.*, CO, CO_2,⋯.

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Unusual Solvatokinetic Behavior of 5-Chlorinated 1,3,3-Spiro(2H-1-Benzopyran-2,2'-Indoline) Derivatives

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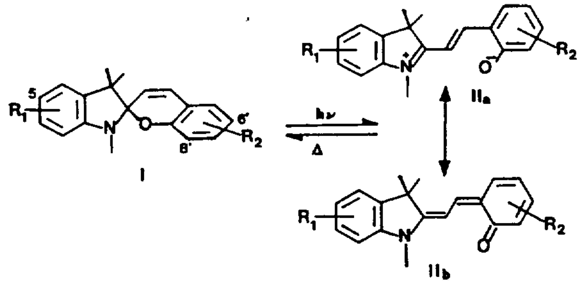
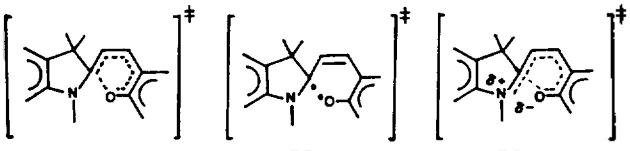
Thermo- and photochromic indolinobenzospiropyran dyes[1] have attracted considerable attention in the last few decades, with regard to various practical applications such as in recording, copying and displaying materials. Spiropyrans are known to be in equilibrium with their metastable colored forms. Absorption of ultraviolet light shifts the equilibrium towards the merocyanine colored form, II, while the reverse process to the colorless form, I, is induced by visible light, heat or spontaneously (Eq. 1). A number of studies[2-4] have reported important advances towards developing spiropyrans for the industrial purpose and understanding of the detailed photochemical processes and the backward spiro-ring formation processes



(1)

Three different mechanistic processes[5] *via* corresponding three transition states ($TS_{1,2\&3}$) have been suggested for the thermal ring closure reaction of the merocyanine open form of spiro-pyrans. TS_1 applies to a concerted electrocyclic process as suggested by Dürr and Ollis *et al.*, TS_2 represents the diradicaloid mechanism formed through homolytic cleavage of the C_2-O bond and is favored by Sueishi *et al.* Finally, TS_3 pertains to the ionic mechanism *via* a merocyanine type zwitterionic species, as suggested by Flannery *et al.*



In recent years, we have reported the solvatokinetic studies[3,4] of the spiro-ring formation from the open-chain merocyanine form of 1,3,3-spiro(2H-1-benzopyran-2,2'-indolines). Excellent linear plots were obtained with negative slopes on plotting log (rate constant) versus the solvent parameter E_T. The large decrease in rate on increasing solvent polarity clearly supported the ionic transition state, TS_3. The diradicaloid TS_2 has been ruled out on the grounds that the colored solutions were unchanged on treatment with radical scavengers such as oxygen, hydrogen and hydroquinone. It is also apparent that the electrocyclic reaction is not expected to show a marked sensitivity to the medium polarity, in accordance with an isopolar, six-membered activated complex.[6]

The present communication reports unusual solvatokinetic behaviors of the 5-chlorinated spirobenzopyrans (**1**-**3**). The influence of substituents in the benzopyran ring on the closure reaction rate in various solvent systems is particular interest since it could yield mechanistic information on the nature of the spiro-ring formation process. Figure 1 shows the doublely branched linear plots for **1** and **2** on plotting log (rate constant) versus the solvent polarity parameter E_T, unlikely to the previous results.[3,4], in which no-branched lin-