Benzofurans from the Seeds of *Styrax obassia*

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*S. obassia* also known as ‘fragrant snowbell’ is a member of the Styracaceae family. It is a shrub or tree native to tropical and subtropical regions with the majority in eastern and southern Asia. The genus *Styrax* is different from other genera of this family due to the production of resinous material, usually secreted when the barks and trunks are injured by sharp objects. This resin, in the past considered as a miraculous remedy in several parts of Asia and America, has been used in traditional medicine to treat inflammatory diseases. Its resin was used by Romans, Egyptians, Phoenicians and Ionians as incense and in therapeutics. The pericarps are used as washing soap (skin elastic material), cough medicine and a piscicidal agent.

Figur e 1. Key HMBC correlations of compound 1.

![Figure 1](image1)

![Figure 2](image2)

Figure 2. Chemical structures of the isolated compounds from the seeds of *S. obassia*.
elucidated as egonol propanoate. Known compounds (2-5) (Figure 2) were identified by comparison of their spectral data with literature values as follow: egonol 6,8,9 (2), egonolacetate 6,8,9 (3), egonol-2-methylbutanoate 6,8,9 (4) and 7-demethoxyegonol-2-methylbutanoate 6,8,9 (5).

### Experimental Section

**General Methods.** Melting points were determined on an Electrothermal IA-9200 melting point apparatus (Electrothermal Engg. Ltd. U.K.) and are uncorrected. Optical rotations were taken on a Jasco P1020 polarimeter. UV spectra were recorded on a Hewlett Packard 8452A Diode Array Spectrophotometer. IR spectra were recorded in KBr with a NEXUS FT-IR spectrophotometer. EIMS and HREIMS were obtained with a JEOL JMS-SX102A spectrophotometer. 1H NMR (500 MHz), 13C NMR (125 MHz), DEPT, COSY, HMQC, and HMBC spectra were obtained with a Varian Unity-Inova 500 spectrophotometer. The NMR samples were prepared in CDCl3/DMSO with tetramethylsilane (TMS) as an internal standard. The chemical shifts and coupling constants (J) were expressed in δ and Hz, respectively. Thin layer chromatography (TLC) was carried out on precoated Silica gel 60 F254 (0.2 mm, Merck, Germany) plates. Preparative thin layer chromatography was carried out on precoated Silica gel 60 F254 (20 × 20 cm², 2.0 mm, Merck, Germany) plates. TLC plates were developed with solvent system A (toluene/ethyl formate/formic acid = 20:2:1, v/v/v) and B (n-hexane/ethyl acetate/toluene = 8:1:1, v/v/v). Developed TLC plates were visualized under UV light at 254 and 365 nm. Silica gel 60 (40-100 μm, Kanto Chemical Co. Japan) was used for the column chromatography. An ADVENTEC SF-1600 was used as the automated fraction collector in the column chromatography.

**Plant Material.** The fruits of S. obassia were collected from Jiri mountain (Hadong-kun) in Kyungnam, Korea in September, 2004 and identified by Dr. Y. H. Kwon (Korea National Arboretum, Pocheon, Korea). A voucher specimen has deposited at the Korea Forest Research Institute, Seoul, Korea.

**Extraction and Isolation.** 8.0 Kg of air-dried and powdered seeds of S. obassia were extracted three times with MeOH at room temperature for 72 hrs each. The combined MeOH extracts were concentrated under vacuum at 40 °C until MeOH was completely removed. The concentrated MeOH extract was dissolved in distilled water and successively partitioned with n-hexane, dichloromethane and ethyl acetate. Column chromatography of an oily mass from n-hexane soluble fraction on silica column gave 93 fractions (250 mL each) in benzeneethyl acetate (2:1, v/v). On the basis of TLC profiles, these fractions are divided into four groups. Group one (46.6 g) was chromatographed on silica gel 60 F254 (20 × 20 cm², 2.0 mm, Merck, Germany) plates. TLC plates were developed with solvent system A (toluene/ethyl formate/formic acid = 20:2:1, v/v/v) and B (n-hexane/ethyl acetate/toluene = 8:1:1, v/v/v). Developed TLC plates were visualized under UV light at 254 and 365 nm. Silica gel 60 (40-100 μm, Kanto Chemical Co. Japan) was used for the column chromatography. An ADVENTEC SF-1600 was used as the automated fraction collector in the column chromatography.
ethyl acetate (5:1, v/v) to give a pure compound 4 (40 mg). The oily mass (43.7 g) upon silica gel column chromatography in n-hexane:ethyl acetate (15:1, v/v) gave 85 fractions (250 mL each). TLC profiles of these fractions led them to divide into four groups. Group one (10.0 g) was chromatographed on silica column in n-hexane:chloroform:ethyl acetate (23:1:1, v/v/v) to give three fractions. Rechromatography of fraction 2 (3.5 g) on silica column with increasing polarity of n-hexane:benzene:ethyl acetate (8:1:1, v/v/v) as an eluent to yield 80 fractions (4.0 g each by a fraction collector). On the basis of TLC profiles these fractions are divided into three parts. Part two (255 mg) was finally chromatographed using chloroform:toluene:ethyl acetate (8:1:1, v/v/v) to give three fractions. Rechromatography of fraction 2 (3.5 g) on silica column in chloroform:toluene:ethyl acetate (17:1:1, v/v/v) gave pure compound 5 (88.8 mg). On the other hand, group four (1.36 g) was chromatographed on silica gel column using n-hexane:toluene:ethyl acetate (5:1, v/v) to give a pure compound 1 (42.7 mg).

The ethyl acetate soluble part (122.7 g) from MeOH extract was chromatographed on silica gel column with increasing polarity of n-hexane:ethyl acetate:acetone (9:2:1→3:2:1→1:2:2, v/v/v) to collect five fractions. Fraction 3 was concentrated to produce a powdery mass which was washed with toluene, benzene and finally with ethyl acetate. The ethyl acetate soluble part produced pure compound 2 (1.08 g).

5-(3"-Propanoyloxypropyl)-7-methoxy-2-(3',4'-methyl-enedioxyphenyl)-benzofuran (1): Colourless crystal, m.p. 86-87°C. [α]D20 +4.7° (c = 0.22, CHCl3). UV (CHCl3) λmax nm (log ε): 242 (3.9), 318 (4.3). IR (KBr) νmax cm−1: 2954, 1738, 1601, 1481, 1371, 1232, 1190, 1038, 941 and 812 cm−1. EIMS m/z 382 ([M]+, base ion), 308, 282, 267 and 251. HREIMS m/z: 382.1416 ([M]+), calcd. for C22H22O6, 382.4141. 1H NMR (CDCl3, 500 MHz), 13C NMR (CDCl3, 125 MHz). COSY and HMBC see Table 1.

Egonol (2): White powder, m.p. 112-113°C (lit.8 113-115°C). EIMS m/z 326 ([M]+). UV, IR, 1H and 13C NMR data are in agreement with literature.6,9,60

Egonolacetate (3): Yellowish powder, m.p. 104-105°C (lit.8 103-105°C). EIMS m/z 368 ([M]+). UV, IR, 1H and 13C NMR data are in agreement with literature.6,9,60

Egonol-2-methylbutanoate (4): Pale yellow oil. EIMS m/z 410 ([M]+). UV, IR, 1H and 13C NMR data are in agreement with literature.6,9,60

7-Demethoxyeygonol-2-methylbutanoate (5): Colourless needles. m.p. 54-55°C (lit.6 55.5-56°C). EIMS m/z: 380 ([M]+). UV, IR, 1H NMR data are in agreement with literature.6,8,9 13C NMR (125 MHz, CDCl3): δ 11.6q (C-4a), 16.6q (C-5a), 26.8t (C-3a), 30.9t (C-2")1, 32.1t (C-1"), 41.1d (C-2"), 63.4t (C-3"), 100.0d (C-3), 101.3r (-O-CH2-0-), 105.4d (C-2"), 108.6d (C-5"), 110.7d (C-7), 119.1d (C-6"), 120.0f (C-4"), 124.5d (C-6), 124.8s (C-1"), 129.5s (C-9), 135.9s (C-5"), 148.0s (C-4"), 148.1s (C-3"), 153.4s (C-8), 156.0s (C-2"), 176.8s, (C-1a).

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