

Phytochemical Study on *Catalpa ovata*

Han Suk Young[†], Min Sun Kim, Hee Juhn Park,
Hae Young Chung and Jae Sue Choi*

College of Pharmacy, Pusan National University, Pusan 609-735

*Dept. of Nutrition and Food Science, National Fisheries

University of Pusan, Pusan 608-737

(Received September 15, 1992)

Abstract □ From the stem bark of *Catalpa ovata*, lupeol, 2(4-hydroxyphenyl)ethyl triacota-noate, a mixture of 9-hydroxy α -lapachone and α -lapachone, 9-methoxy α -lapachone, feru-lic acid, 6-feruloyl catalpol, catalposide and 6'-feruloyl sucrose were isolated and identified.

Keywords □ *Catalpa ovata*, Bignoniaceae, lupeol, 6-O-feruloyl catalpol, 6'-O-feruloyl sucrose.

Catalpa ovata G. Don (Bignoniaceae) is a deci-duous tall tree which is grow naturally in Korea and China, and the stem bark have been used as a Chinese crude drug for the treatment of fever, jaundice, intoxication and eczema¹⁾. It was recently found that a methanol extract caused a significant antimutagenic in Ame's test with *Salmonella typhi-murium* strain TA 100 in the presence of råt liver homogenate (S 9 mix)²⁾. Previous authors reported the isolation of *p*-coumaric acid and ferulic acid from the stem bark of *C. ovata*³⁾. This paper deals with the isolation and identification of constituents from this plant part.

EXPERIMENTAL METHODS

All melting point were measured on an Electro-thermal digital melting point apparatus and are un-corrected. The IR spectra were determined in KBr tablets on a Bomem MB-100 FT-IR spectrophoto-meter and the UV spectra were runned Tegimenta Uvicon 990 UV spectrophotometer. The ¹H- and ¹³C-NMR spectrometer using TMS as an internal standard. The FAB mass spectra were taken with Kratos MS 25 RFA spectrometer. The MS spectra were taken with Jeol, JMS D-300 spectrometer. For TLC, Kieselgel 60 F₂₅₄ sheets (Merck) were used.

[†]To whom all correspondence should be addressed

Plant material

Shade-dried stem bark of *Catalpa ovata* was col-lected at Dugu Dong, Pusan, in August 1990. A voucher specimen is deposited in the herbarium of the Pusan National University.

Extraction, fractionation and isolation

The dried stem bark (3.5 kg) of *Catalpa ovata* was extracted with MeOH under reflux. The MeOH ex-tract was partitioned with *n*-hexane, CHCl₃, EtOAc, BuOH and H₂O as shown in Chart 1. The *n*-hexane extract (50g) was chromatographed over silica gel (1.2 kg) using *n*-hexane : EtOAc (gradient) to give **1**, **2** and a mixture of **3** and **4**. The CHCl₃ extract (35g) was chromatographed over silica gel (800g) using CHCl₃ : MeOH : H₂O (25 : 8 : 5) to give frac-tions 1 and 2 and further chromatographed to af-ford compound **5** from fraction 1 and compound **6** from fraction 2. The BuOH extract (65g) was chromatographed over silica gel (1.4 kg) using CHCl₃ : MeOH : H₂O (7 : 3 : 1) to give **7**, **8** and **9** in the order of elution.

Compound 1, lupeol

mp.: 215° IR ν_{max}^{KBr} (cm⁻¹): 3339 (broad, OH), 2928, 2849 (aliphatic C-H), ¹H-NMR (300 MHz, CDCl₃) δ : 0.76, 0.79, 0.83, 0.94, 0.96, 1.03 (each 3H, s, CH₃), 1.68 (3H, s, 30-CH₃), 3.19 (1H, m, C₃-H), 4.56 (1H, t-like, H α -29), 4.69 (H, d-like, H β -29), ¹³C-NMR (75.5

MHz, CDCl₃) δ: 38.7 (C-1), 27.4 (C-2), 79.0 (C-3), 39.0 (C-4), 55.3 (C-5), 18.3 (C-6), 34.3 (C-7), 40.8 (C-8), 50.4 (C-9), 37.1 (C-10), 20.9 (C-11), 25.1 (C-12), 38.0 (C-13), 42.8 (C-14), 27.4 (C-15), 35.6 (C-16), 42.9 (C-17), 48.0 (C-18), 47.9 (C-19), 150.9 (C-20), 29.8 (C-21), 39.9 (C-22), 27.9 (C-23), 15.4 (C-24), 16.1 (C-25), 15.9 (C-26), 14.5 (C-27), 18.0 (C-28), 109.3 (C-29), 19.3 (C-30), MS (*m/z*, rel. int): 426 ([M, C₃₀H₅₀O]⁺, 33.6), 411 ([M-CH₃]⁺, 6.7), 393 ([M-H₂O]⁺, 1.6), 383 ([M-isopropyl]⁺, 1.6), 315 (7.0), 299 (1.7), 272 (3.2), 257 (5.4), 247 (4.3), 234 (8.5), 218 (24.9), 207 (36.4), 189 (41.3), 55 (100).

Compound 2, 2-(4-hydroxyphenyl) ethyl triacontanoate

mp.: 83-83.5°, IR ν_{\max}^{KBr} (cm⁻¹): 3350 (broad, OH), 2917, 2848 (aliphatic C-H), 1734 (ester), 1653, 1559, 1518 (aromatic C=C), ¹H-NMR (300 MHz, CDCl₃) δ: 0.87 (3H, t, *J*=6.30 Hz, CH₃), 1.25 (methylene), 2.31 (2H, m, C α -H to carbonyl), 2.85 (2H, t, *J*=7.0 Hz, H-8'), 4.23 (2H, t, *J*=7.0 Hz, H-7'), 6.76 (2H, d, *J*=8.40 Hz, H-2', 6'), 7.07 (2H, d, *J*=8.40 Hz, H-3', 5'), 9.40 (OH), ¹³C-NMR (75.5 MHz, CDCl₃) δ: 14.0 (C-30), 22.6 (C-29), 25.0 (C-3), 29.3 (C-4), 29.5 (C-5), 32.9 (C-28), 34.3 (C-2), 34.5 (C-7'), 65.0 (C-8'), 115.3 (C-2', 6'), 130.0 (C-3', 5'), 154 (C-4'), 173.9 (C-1), MS (*m/z*, rel. int): no molecular ion peak, 452 ([C₃₂H₆₃O]⁺, 6.9), 424 (27.5), 396 (52.9), 368 (71.6), 340 (26.5), 312 (8.8), 284 (2.9), 256 (4.9), 121 ([C₈OH₉]⁺, 36.2), 120 ([121-H]⁺, 100).

A mixture of compounds 3 and 4

Compounds 3 and 4 were separated by GC/MS. Condition: analyzer: quadrupole mass filter (203 nm), ionization potential; 70 eV, column; cross-linked fused silica capillary column (HP) HP-5, 25 m×0.2 mm×0.33 μm, inj. temp.: 280°C, oven; 100°C (3 min) 15°/min, 280°C (15 min), carrier gas; He, flow rate; 1 ml/min, split ratio; 1/25, Compound 3 (9-hydroxy- α -lapachone) (*m/z*, rel. int.); *m/z* 258 ([M]⁺, 71), 243 ([M-CH₃]⁺, 100), 230 ([M-CO]⁺, 5), 175 ([230-C₄H₁₁]⁺, 40), 215 ([243-CO]⁺, 15), Rt. 15.46 min, compound 4 (α -lapachone) (*m/z*, rel. int.); *m/z* 242 ([M]⁺, 50), 227 ([M-CH₃]⁺, 100), 214 ([M-CO]⁺, 6), Rt. 14.78 min.

Compound 5, 9-methoxy- α -lapachone

Amorphous powder, IR ν_{\max}^{KBr} (cm⁻¹): 2921 (C-H), 1676 (α , β -unsaturated ketone), 1623, 1584, 1472 (aromatic C=C), UV $\lambda_{\max}^{\text{CHCl}_3}$ nm (log ϵ): 380 (3.22),

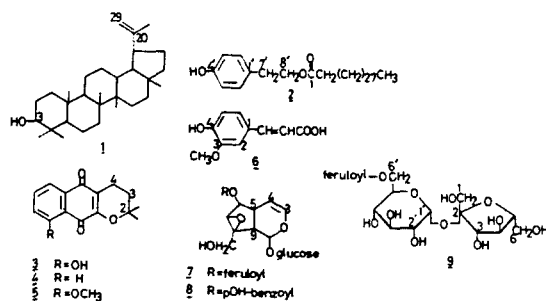


Fig. 1. Structures of isolated compounds 1-9.

292 (3.31), ¹H-NMR (80 MHz, CDCl₃) δ: 1.40 (6H, s, C₂-gem. methyl), 1.78 (2H, t, *J*=6.42 Hz, H-3), 2.58 (2H, t, *J*=6.42 Hz, H-4), 3.97 (3H, s, OCH₃), 7.28-7.73 (3H, aromatic H), MS (*m/z*, rel. int): 272 ([M]⁺, 100), 257 ([M-Me]⁺, 77.3), 244 ([M-CO]⁺, 10), 240 ([M-CH₃OH]⁺, 50), 229 ([M-isopropyl]⁺, 28.9), 216 ([M-2CO]⁺, 55), 216 ([M-C₄H₈]⁺, 12.8), 189 ([M-C₆H₁₀]⁺, 79.1).

Compound 6, trans-ferulic acid

mp.: 174°, UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 236 (4.07), 300 (3.97, sh), 322 (4.21), $\lambda_{\max}^{\text{MeOH} + \text{NaOMe}}$ nm (log ϵ): 238 (4.00), 304 (3.97, sh), 348 (4.32), IR ν_{\max}^{KBr} (cm⁻¹): 3424 (broad, OH), 2903 (C-H), 1670 (α , β -unsaturated ketone), 1649, 1549 (aromatic C=C), ¹H-NMR (300 MHz, CDCl₃+DMSO-d₆) δ: 3.82 (s, OCH₃), 6.35 (1H, d, *J*=15.80 Hz, H- α), 6.79 (1H, d, *J*=8.10 Hz, H-5), 7.07 (1H, dd, *J*=8.10 & 1.70 Hz, H-6), 7.27 (1H, d, *J*=1.70 Hz, H-2), 7.49 (1H, d, *J*=15.80 Hz, H- β), 9.49 (br. s, OH), 12.07 (br. s, COOH), ¹³C-NMR (75.5 MHz, CDCl₃+DMSO-d₆) δ: 125.8 (C-1), 111.2 (C-2), 147.9 (C-3), 149.0 (C-4), 115.5 (C-5), 122.7 (C-6), 167.9 (C=O), 55.7 (OCH₃), 144.4 (C β), 115.6 (C α), MS (*m/z*, rel. int): 194 ([M]⁺, 100), 179 ([M-CH₃]⁺, 18), 151 (6), 133 (17), 123 (6).

Compound 7, 6-O-trans-feruloyl catalpol

Amorphous powder, UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 236.2 (4.06), 300.2 (4.18), 327.0 (4.33), $\lambda_{\max}^{\text{MeOH} + \text{NaOMe}}$ nm (log ϵ): 247.0 (4.26), 300.2 (4.18), 381.0 (4.36), IR ν_{\max}^{KBr} (cm⁻¹): 3400 (broad, OH), 2926 (aliphatic C-H), 1701 (α , β -unsaturated ketone), 1655 (C=C), 1631, 1597, 1516 (aromatic), 1269, 1160 (methylene), 1100-1000 (glycosidic C-O), ¹H-NMR (300 MHz, DMSO-d₆) δ: 2.68 (1H, dd, *J*=7.9 Hz, 9.3 Hz, H-9), 3.40-3.50 (H-2'~H-5'), 3.73 (1H, br. s, H-7), 3.79 (OCH₃),

3.76-3.92 (1H, m, H-6'), 4.27, 3.80 (each, 1H, d, $J = 13.30$ Hz, H-10), 4.87 (1H, d, $J = 7.80$ Hz, H-1'), 4.95 (1H, d, $J = 7.70$ Hz, H-6), 5.06 (1H, d, $J = 9.50$ Hz, H-1), 6.20 (1H, d, $J = 15.90$ Hz, H α), 6.36 (1H, d, $J = 5.70$ Hz, H-3), 6.82 (1H, d, $J = 8.2$ Hz, H-6''), 6.96 (1H, d, $J = 8.2$ Hz, H-5''), 7.00 (br. s, H-2''), 7.49 (1H, d, $J = 15.9$ Hz, H β), $^{13}\text{C-NMR}$ (75.5 MHz, DMSO- d_6) δ : 92.9 (C-1), 141.1 (C-3), 101.6 (C-4), 35.0 (C-5), 79.1 (C-6), 58.5 (C-7), 65.6 (C-8), 41.7 (C-9), 61.3 (C-10), 97.0 (C-1'), 73.3 (C-2'), 77.4 (C-3'), 70.2 (C-4'), 76.4 (C-5'), 65.6 (C-6'), 166.6 (C=O), 113.8 (H- α), 147.9 (H- β), 125.5 (C-1''), 111.1 (C-2''), 147.9 (C-3''), 149.5 (C-4''), 115.5 (C-5''), 123.4 (C-6''), FAB-MS (m/z , rel. int): 561 ($[\text{M} + \text{Na}]^+$, 13), 237 (47), 221 (53), 177 (feruloyl, 100).

Compound 8, catposide

Amorphous powder, IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 3415 (OH), 2905 (aliphatic CH), 1697 (α , β -unsaturated ketone), 1632 (C=C), 1600, 1517 (aromatic C=C), 1457 (CH_3), 1275, 1169 (methylene), 1031 (glycosidic C-O), $^1\text{H-NMR}$ (300 MHz, $\text{D}_2\text{O} + \text{CD}_3\text{OH}$) δ : 2.34 (1H, m, H-5), 2.72 (1H, m, H-9), 3.3-3.5 (H-2'~H-5'), 3.78 (1H, d, $J = 11.0$ Hz, H $_{10b}$), 3.86 (1H, br. s, H-7), 3.96 (1H, d, $J = 20.90$ Hz, H $_{10a}$), 4.77 (1H, d, $J = 7.80$ Hz, anomeric proton), 4.98-5.02 (H-1), 5.14 (1H, m, H-4), 5.62 (1H, d, $J = 3.70$ Hz, H-6), 6.32 (1H, m, H-3), 6.92 (2H, d, $J = 8.80$ Hz, H-3'', 5''), 7.92 (2H, d, $J = 8.80$ Hz, H-2'', 6''), $^{13}\text{C-NMR}$ (75.5 MHz, DMSO- d_6) δ : 92.9 (C-1), 141.0 (C-3), 101.7 (C-4), 35.0 (C-5), 80.3 (C-6), 58.5 (C-7), 66.0 (C-8), 42.0 (C-9), 61.0 (C-10), 97.8 (C-1'), 73.4 (C-2'), 77.0 (C-3'), 70.2 (C-4'), 76.3 (C-5'), 61.4 (C-6'), 165.5 (C=O), 119.8 (C-1''), 131.6 (C-2''), 114.7 (C-3''), 162.2 (C-4''), 115.4 (C-5''), 123.1 (C-6'').

Compound 9, 6'-trans-feruloyl sucrose

White powdery crystal from acetone, mp.: 143°, IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 3365 (broad, OH), 2931 (aliphatic CH), 1699 (α , β -unsaturated ketone), 1633 (C=C), 1597, 1518 (aromatic), 1100-1000 (glycosidic C-O), UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 327, 300 (sh), $^1\text{H-NMR}$ (300 MHz, DMSO- d_6) δ : 5.23 (1H, d, $J = 3.6$ Hz, H-1'), 5.24 (1H, br. s, H-4 OH), 5.12 (1H, d, $J = 5.60$ Hz, H-2' OH), 5.03 (1H, d, $J = 5.42$ Hz, H-4' OH), 4.87 (1H, d, $J = 4.06$ Hz, H-3' OH), 4.81 (1H, t, $J = 5.86$ Hz, H-1 $_{ab}$, OH), 4.59 (1H, d, $J = 7.4$ Hz, H-3 OH), 4.43 (1H, t, $J = 5.14$ Hz, H-6 $_{ab}$ OH), 4.31 (1H, dd, $J = 11.0$ Hz and 1.60 Hz, H-6 $_b$), 4.12 (1H, dd, $J = 11.70$ Hz

and 6.36 Hz, H-6 $_a$), 3.94 (1H, dd, $J = 9.90, 6.10, 1.80$ Hz, H-5'), 3.91 (1H, d, $J = 7.90$ Hz, H-3), 3.81 (3H, s, OCH_3), 3.77-3.82 (2H, overlapped, H-4 and H-5), 3.58-3.64 (2H, overlapped, H-6 a, b), 3.52 (1H, dd, $J = 9.60$ and 3.60 Hz, H-3'), 3.40 (2H, d, $J = 5.50$ Hz, H-1a, b), 3.24 (1H, dd, $J = 9.60$ Hz and 3.60 Hz, H-2'), 3.12 (1H, dt, $J = 9.60$ Hz and 4.80 Hz, H-4'), $^{13}\text{C-NMR}$ (75.5 MHz, D_2O) δ : 63.8 (C-1), 103.8 (C-2), 82.6 (C-3), 77.0 (C-4), 74.5 (C-5), 62.6** (C-6), 91.3 (C-1'), 72.8* (C-2'), 71.5 (C-3'), 70.2 (C-4'), 70.0 (C-5'), 62.4 (C-6'), 125.6 (C-1''), 111.1 (C-2''), 147.9 (C-3''), 149.3 (C-4''), 115.4 (C-5''), 123.1 (C-6''), 114.4 (H α), 144.9 (H β), 166.6 (C=O), FAB-MS (m/z , rel. int): 541 ($[\text{M} + \text{Na}]^+$, 14), 237 (26), 177 (feruloyl, 48), 131 (100).

Acetylation of compounds 7 and 9

Fifty mg of 7 and 9 in pyridine and Ac_2O (2 ml, each) was separately allowed to stand at room temperature. The reaction mixtures were poured into crushed ice and filtered to give 7a and 9a, respectively.

7a: IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): no OH, 2352, 1754, 1636, 1509, 1372, 1231, 1155, 1047 (glycosidic C-O), $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 2.02 (3H, s, OAc), 2.04, 2.13 (each, 6H, s, OAc), 2.32 (3H, s, OAc, linked to aromatic ring), 2.63-2.72 (2H, m, H-5 and H-9), 3.72-3.75 (1H, m, H-5'), 3.73 (1H, br. s, H-7), 3.87 (OCH_3), 4.00 (1H, d, $J = 12.70$ Hz, H-10), 4.21-4.32 (1H, dd, $J = 4.10$ and 12.40 Hz, H-6'), 4.85-4.90 (1H, m, H-2'), 4.88 (1H, H-10), 4.97-5.03 (4H, m, H-4, 4', 6, 1'), 5.14 (1H, t, $J = 9.50$ Hz, H-3'), 5.27-5.20 (1H, m, H-1), 6.33 (1H, d, $J = 5.90$ Hz, H-3), 6.44 (1H, d, $J = 16.0$ Hz, H- α), 7.06-7.13 (2H, dd, $J = 8.0$ Hz, H-5'', 6''), 7.12 (1H, s, H-2''), 7.70 (1H, d, $J = 16.0$ Hz, H- β), 9a: IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): no OH, 2962 (aliphatic CH), 1750 (ester), 1638, 1510, 1424 (aromatic C=C), 1373, 1232, 1156, 1121, 1043 (glycosidic C-O), $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.67 (1H, d, $J = 15.95$ Hz, H β), 7.17 (1H, d, $J = 1.60$ Hz, H-2''), 7.15 (1H, dd, $J = 1.60$ and 8.10 Hz, H-6'), 7.04 (1H, d, $J = 8.10$ Hz, H-5'), 6.48 (1H, d, $J = 15.95$ Hz, H α), 5.70 (1H, d, $J = 3.70$ Hz, H-1'), 5.48 (1H, t, $J = 9.80$ Hz, H-3'), 5.45 (1H, d, $J = 5.70$ Hz, H-3), 5.36 (1H, d, $J = 5.70$ Hz, H-4), 5.12 (1H, t, $J = 9.80$ Hz, H-4'), 4.90 (1H, dd, $J = 3.60$ and 10.20 Hz, H-2'), 4.20-4.40 (8H, H-1, 5, 5', 6, 6'), 3.88 (s, OCH_3), 2.32 (3H, s, OAc, linked to aromatic ring), 2.18 (3H, s, OAc), 2.06 (6H, s, $\text{OAc} \times 2$), 2.02 (3H, s, OAc), 2.10 (9H, s, $\text{OAc} \times 3$)

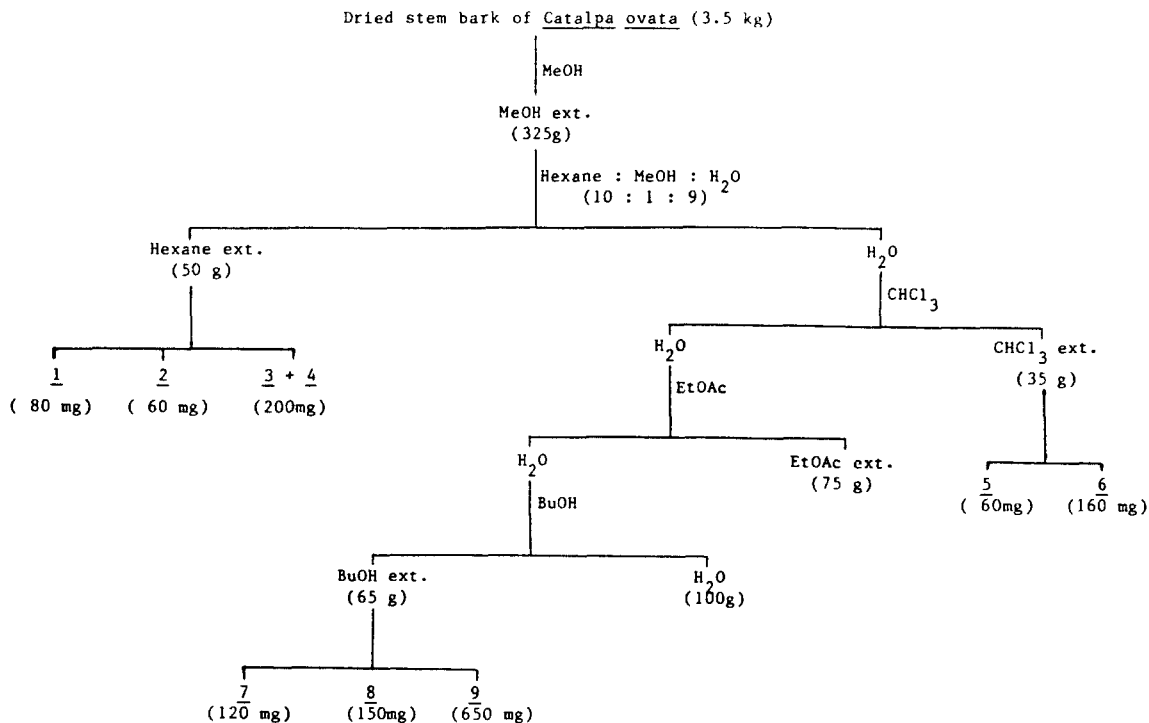


Chart I. Extraction, fractionation and isolation of *Catalpa ovata*

Alkaline hydrolysis of compounds 7 and 9

It was carried out by refluxing with 3% KOH in MeOH for 3 hr and diluted with water, extracted with EtOAc, concentrated to give hydrolyzed product. Compound 7 contains methyl ferulate and catalpol. Compound 9 contains methyl ferulate and sucrose. These were identified by comparison of the TLC with those of an authentic sample.

RESULTS AND DISCUSSION

Silica gel column chromatography of the hexane, CHCl_3 , BuOH soluble portions of the methanol extract yielded nine compounds 1-9 as shown in Chart I.

Compound 2-6 and 8 were readily elucidated as 2(4-hydroxyphenyl)ethyl triacontanoate 2, a mixture of 9-hydroxy α -lapachone 3 and α -lapachone 4, 9-methoxy α -lapachone 5, ferulic acid 6 and catalposide 8 respectively, by comparison of their physical properties and spectral data with those reported in the wood of this plant^{4,5}.

Compound 1, mp. 215°C showed positive Lieber-

mann-Burchard test and identified as lupeol from its molecular ion peak at m/z 426 and NMR spectral data. It was further identified by comparison with an authentic sample (TLC and mmp).

Compound 7 showed positive results in Molisch test besides iridoid color reaction (dark brown in dil. H_2SO_4) and showed absorption bands at 236.2, 300.2 and 327.0 nm ($\log \epsilon$ 4.06, 4.18 and 4.33), which were shifted by addition of NaOMe (247.0, 300.2, 381.0 nm ($\log \epsilon$ 4.26, 4.18, 4.36)). Its IR also exhibited the presence of a hydroxyl group (3400 cm^{-1}), α , β -unsaturated ketone group (1710 cm^{-1}), a double bond (1655 cm^{-1}), aromatic ring systems ($1631, 1597, 1516 \text{ cm}^{-1}$) and a glycoside bond ($1100-1000 \text{ cm}^{-1}$), indicating that compound 7 was iridoid glycoside containing phenolic hydroxyl group. The $^1\text{H-NMR}$ spectrum showed typical proton signals of a feruloyl [δ 7.49, 6.20 (each 1H, d, $J=15.90$ Hz), 7.00 (1H, br. s), 6.96 (1H, d, $J=8.20$ Hz), 6.82 (1H, d, $J=8.20$ Hz), 3.79 (OCH_3)], catalpol (see experimental) moieties and anomeric proton signals at δ 4.87 (1H, d, $J=7.80$ Hz).

Alkaline hydrolysis of 7 afforded methyl ferulate

and catalpol which were identified by TLC in comparison to authentic samples.

These data indicated that compound **7** was a feruloyl ester of catalpol. The FAB mass spectrum of **7** supported this finding showing a quasimolecular ion peak at m/z 561 $[M+Na]^+$ and prominent base ion peak at 177 [feruloyl, 100%]. The NMR spectra provided information for the establishment of the position of the acyl moiety. Comparison of the 1H -NMR spectrum of compound **7** with that of catalpol⁶ showed signals with almost identical chemical shifts and coupling constant values, with the exception of the H-6 signal which is downfield-shifted to 4.95 ppm, indicating an acylation in this position. This was further confirmed by the inspection of ^{13}C -NMR spectroscopy (see experimental). The chemical shift values were almost identical to the NMR data of 6-O-feruloylcatalpol reported only in the literature⁷. Thus, the structure of **7** was elucidated as 6-trans-feruloylcatalpol. This is the second report of the occurrence in nature.

Compound **9** was obtained as a white amorphous powder and exhibited the presence of a hydroxyl group (3365 cm^{-1}), α , β -unsaturated ketone group (1699 cm^{-1}), a double bond (1633 cm^{-1}) and aromatic ring systems (1597 , 1518 cm^{-1}) in its IR spectrum. The 1H -NMR spectrum showed typical proton signals of a feruloyl [δ 7.57, 6.34 each 1H, d, $J=16.0$ Hz), 7.15 (1H, d, $J=2.0$ Hz), 7.11 (1H, dd, $J=8.20$ & 2.0 Hz), 6.90 (1H, d, $J=8.20$ Hz), 3.86 (OCH₃)] and sucrose (see experimental) moieties.

Acetylation of **9** with acetic anhydride in pyridine yielded the corresponding peracetate (**1a**), the 1H -NMR spectrum of which showed an aromatic acetoxy and seven alcoholic acetoxy signals indicating the presence of one mole of ferulic acid and sucrose in **9**.

Hydrolysis of **9** with 3% sodium methoxide solution afforded methyl ferulate and sucrose, confirming its constituents. Thus, the fundamental structure of **9** was indicative of a feruloyl ester of sucrose. The FAB mass spectrum of **9** supported this finding showing a quasimolecular ion peak at m/z 541 $[M+Na]^+$. The NMR spectra provided information for the establishment of the position of the acyl moiety. In the NMR spectra, the signals for the sucrose H₂(C)-6' were displaced downfield by acylation compared with those of sucrose (see Table I).

Table I. ^{13}C -NMR spectral data of sucrose and compound **9** in DMSO- d_6

Compound Carbon No.	Sucrose ¹⁹⁾	9 (sugar part)
C-1	62.15	62.1
2	104.07	103.9
3	77.26	79.9
4	74.44	74.4
5	82.56	82.5
6	62.21	62.4
C-1'	91.76	91.6
2'	71.67	71.4
3'	72.96	72.6
4'	69.98	70.2
5'	72.83	70.0
6'	60.64	63.6

Therefore, the structure of **9** was determined to be 6'-O-feruloylsucrose, previously known only from *Lilium speciosum*⁸⁾. The occurrence of conjugates containing sucrose is limited to several groups of plants i.e., Polygonaceae⁹⁾, Polygalaceae¹⁰⁾, Brassicaceae¹¹⁾, Rosaceae¹²⁾ and especially in Liliaceae^{8,13-18)} in spite of the widespread occurrence of phenylpropanoids and sucrose. This is the first report of the occurrence of sucrose esters in Bignoniaceae family.

ACKNOWLEDGEMENT

This study was supported in part by a grant (90-0500-03) from KOSEF.

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