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Studies on the Constituentes of *Lespedeza cyrtobotrya* Miq. I. The Structures of a New Chalcone and Two New Isoflav-3-ens

Toshio Miyase, Akira Ueno, Tadataka Noro, and Seigo Fukushima

Shizuoka College of Pharmacy[1]

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The bark of *Lespedeza cyrtobotrya* Miq. afforded a new chalcone, lespeol (I), together with xanthoangelol (II). The heartwood of *Lespedeza cyrtobotrya* Miq. afforded two new isoflav-3-ens, haginin A (IIIa) and B (IVa), together with genistein, daidzein, dalbergioidin, 3,9-dihydroxypterocarp-6a-en and isoliquiritigenin. The structures were established on the basis of chemical and spectral data.

Keywords——*Lespedeza cyrtobotrya* Miq.; lespeol; xanthoangelol; haginin A; haginin B; 3,9-dihydroxypterocarp-6a-en; genistein; daidzein; dalbergioidin; isoliquiritigenin

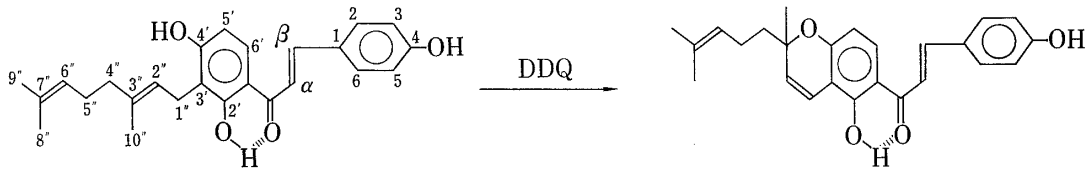
We have already reported the structures of new isoflavanones, lespedeol A[2] and lespedeol B,[3] and new pterocarpans, lespein and lespedezin,[4] isolated from the root bark of *Lespedeza homoloba* Nakai (Japanese name Tsukushihagi). The woody plants of *Lespedeza* are easy to hybridize, and in connection with this, we investigated *Lespedeza cyrtobotrya* Miq. (Japanese name Marubahagi) as part of a search for isoflavonoids. A new chalcone, lespeol (I), was isolated from the ethyl acetate-soluble fraction of a methanolic extract of the bark together with xanthoangelol (II). Two new isoflav-3-ens, haginin A (IIIa) and B (IVa), were isolated from the ether-soluble fraction of a methanolic extract of the heartwood together with genistein, daidzein, dalbergioidin and 3,9-dihydroxypterocarp-6a-en. Isoliquiritigenin was isolated from the ethyl acetate-soluble fraction of a methanolic extract of the heartwood.

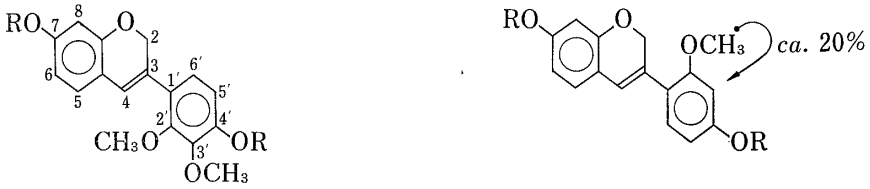
Lespeol (I), $C_{25}H_{26}O_4$, M^+ 390.1838 (Calcd for $C_{25}H_{26}O_4$ 390.1836) was isolated as an orange-yellow viscous oil, which gave positive ferric chloride and magnesium-hydrochloric acid reactions. It gave a red color reaction with sulfuric acid. The infrared (IR) spectrum suggested the presence of hydroxyl groups (3260 cm^{-1}) and a hydrogen-bonded aromatic ketone (1630 cm^{-1}), while the ultraviolet (UV) spectrum suggested the chalcone skeleton,[5] showing absorption maxima at 229 (4.28), 280 (4.07) and 371 (4.53) nm (log ε). The nuclear magnetic resonance (NMR) spectrum was closely related to that of xanthoangelol (II)[6] and showed A_2B_2-type proton signals on an aromatic ring at δ 6.84 (2H, d, J=9 Hz) and δ 7.50 (2H, d, J=9 Hz). In the olefinic proton region of I, three AB-type proton signals were observed, δ 6.35 (1H, d, J=9 Hz) and δ 7.67 (1H, d, J=9 Hz); δ 5.52 (1H, d, J=10 Hz) and δ 6.77 (1H, d, J=10 Hz); δ 7.38 (1H, d, J=15 Hz) and δ 7.80 (1H, d, J=15 Hz). The last signals were assigned to *trans* olefinic protons adjoining a carbonyl group. A chelated hydroxyl group was observed at δ 13.73. The signals of a methyl proton attached to the ether carbon and two methyl protons attached to the double bond appeared at δ 1.42 (3H, s), δ 1.56 (3H, s) and δ 1.65 (3H, s) respec-

1) Location: *2-2-1, Oshika, Shizuoka, 422, Japan.*
2) A. Ueno, M. Ichikawa, T. Miyase, S. Fukushima, Y. Saiki, and K. Morinaga, *Chem. Pharm. Bull.*, **21**, 1734 (1973).
3) A. Ueno, M. Ichikawa, S. Fukushima, Y. Saiki, and K. Morinaga, *Chem. Pharm. Bull.*, **21**, 2712 (1973).
4) A. Ueno, M. Ichikawa, S. Fukushima, Y. Saiki, T. Noro, K. Morinaga, and H. Kuwano, *Chem. Pharm. Bull.*, **21**, 2715 (1973).
5) T. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, New York, 1970, p. 227.
6) M. Kozawa, N. Morita, K. Baba, and K. Hata, *Chem. Pharm. Bull.*, **25**, 515 (1977); K. Kozawa, N. Morita, K. Baba, and K. Hata, *Yakugaku Zasshi*, **98**, 210 (1978).

tively. An olefinic and two methylenic proton signals appeared at δ 5.08 (1H, m), δ 1.72 (2H, m) and δ 2.06 (2H, m) respectively. Comparison of these data with those of xanthoangelol (II) suggested I to be an oxidatively cyclized derivative of II, and this was confirmed by the synthesis[3] of I from II with 2.3-dichloro-5,6-dicyano-1,4-benzoquinone.

Haginin A (IIIa), $C_{17}H_{16}O_5$, was isolated as colorless needles, mp 130.5—131.5°, and gave positive ferric chloride and diazo reactions. The IR spectrum suggested the presence of hydroxyl groups (3380 cm^{-1}) and aromatic rings (1610, 1585, 1505, 1472 cm^{-1}), while the UV spectrum suggested the isoflav-3-en,[7,8] showing absorption maxima at 237 sh (4.23), 300 sh (4.21) and 322 (4.32) nm (log ε). The mass (MS) spectrum showed major ions at *m/e* 300 (M^+, 100), 285 (M^+-CH_3, 34) and 270 ($M^+-2\times CH_3$, 17). The NMR spectrum showed the signals of two methoxyl groups at δ 3.80 (3H, s) and δ 3.82 (3H, s), two hydroxyl groups at δ 8.03 and δ 8.38, AB-type proton signals on an aromatic ring at δ 6.94 (d, J=8 Hz) and δ 6.65 (1H, d, J=8 Hz), and ABX-type proton signals on an aromatic ring at δ 6.34 (1H, d, J=2 Hz),





IIIa: R=H
IIIb: R=Ac
IIIc: R=Me

IVa: R=H
IVb: R =Ac

Chart 1

TABLE I. NMR Data for IIIa and IIIb

	C_2–H	C_4–H	C_5–H	C_6–H
IIIa (acetone-d_6)	4.93 d, J=1 Hz	6.56 br. s	6.94 d, J=8 Hz	6.41 dd, J=8 Hz J=2 Hz
IIIb ($CDCl_3$)	4.98 d, J=1 Hz	6.53 br. s	6.85 d, J=8 Hz	6.60 dd, J=8 Hz J=2 Hz
Δ (IIIb−IIIa)	+0.05	−0.03	−0.09	+0.19

	C_8–H	$C_{5'}$–H	$C_{6'}$–H	OH or OAc	OMe
IIIa (acetone-d_6)	6.34 d, J=2 Hz	6.65 d, J=8 zH	6.94 d, J=8 Hz	8.03 8.38	3.80 3.82
IIIb ($CDCl_3$)	6.56 d, J=2 Hz	6.85 d, J=8 Hz	6.97 d, J=8 Hz	2.24 2.30	3.79 3.83
Δ (IIIb−IIIa)	+0.22	+0.20	+0.03		

7) R.B. Bradabury and D.E. White, *J. Chem. Soc.*, **1953**, 871.
8) T. Kinoshita, T. Saitoh, and S. Shibata, *Chem. Pharm. Bull.*, **24**, 991 (1976).

δ 6.41 (1H, dd, J=8 Hz, J=2 Hz) and δ 6.94 (d, J=8 Hz). Furthermore, the NMR spectrum showed A_2X-type proton signals at δ 4.93 (2H, d, J=1Hz) and δ 6.56 (1H, br.s), which are characteristic of isoflav-3-en.[8-10] On acetylation with acetic anhydride and pyridine, IIIa gave the diacetate (IIIb), $C_{21}H_{20}O_7$, mp 130—132°, and its NMR spectrum showed two acetoxyl proton signals on an aromatic ring at δ 2.24 (3H, s) and δ 2.30 (3H, s), AB-type proton signals on an aromatic ring at δ 6.97 (1H, d, J=8 Hz) and δ 6.85 (1H, d, J=8 Hz) and ABX-type proton signals on an aromatic ring at δ 6.56 (1H, d, J=2 Hz), δ 6.60 (1H, dd, J=8 Hz, J=2 Hz) and δ 6.85 (1H, d, J=8 Hz). Acetylation of IIIa resulted in downfield shifts of Δ 0.20 ppm for the proton at δ 6.65, Δ 0.22 ppm for the proton at δ 6.34 and Δ 0.19 ppm for the proton at δ 6.41. On methylation with diazomethane, IIIa gave the dimethylether (IIIc), $C_{19}H_{20}O_5$, mp 102—103° and its NMR spectrum showed four methoxyl proton signals at δ 3.70 (3H, s), δ 3.79 (3H, s), δ 3.80 (3H, s) and δ 3.82 (3H, s). These data for IIIc were in good agreement with those of tri-O-methyl sepiol, which was synthesized from sepiol isolated from *Gliricidia sepium* by Lurd *et al.*[10] IIIa was hydrogenated over palladium–charcoal to give an isoflavan (IIId), $C_{17}H_{18}O_5$, mp 156—157.5°. The NMR spectrum showed characteristic ABMXX′-type proton signals of C_2-H_2, C_3-H and C_4-H_2 of an isoflavan[10-12] skeleton at δ 3.92, δ 4.15, δ 3.43, δ 2.80 and δ 2.83, respectively. The MS spectrum of IIId showed major ions at *m/e* 302 (M^+, 100), 180 (13), 179 (93), 167 (52), 166 (37), 164 (52) and 122 (20). The ions 180 and 122, derived from a retro Diels-Alder fragmentation (Chart 2),[13,14] suggested that a hydroxyl group was attached to the A ring and that a hydroxyl and two methoxyl groups were attached to the B ring. No nuclear Overhauser effect (NOE) was observed at the aromatic proton signals

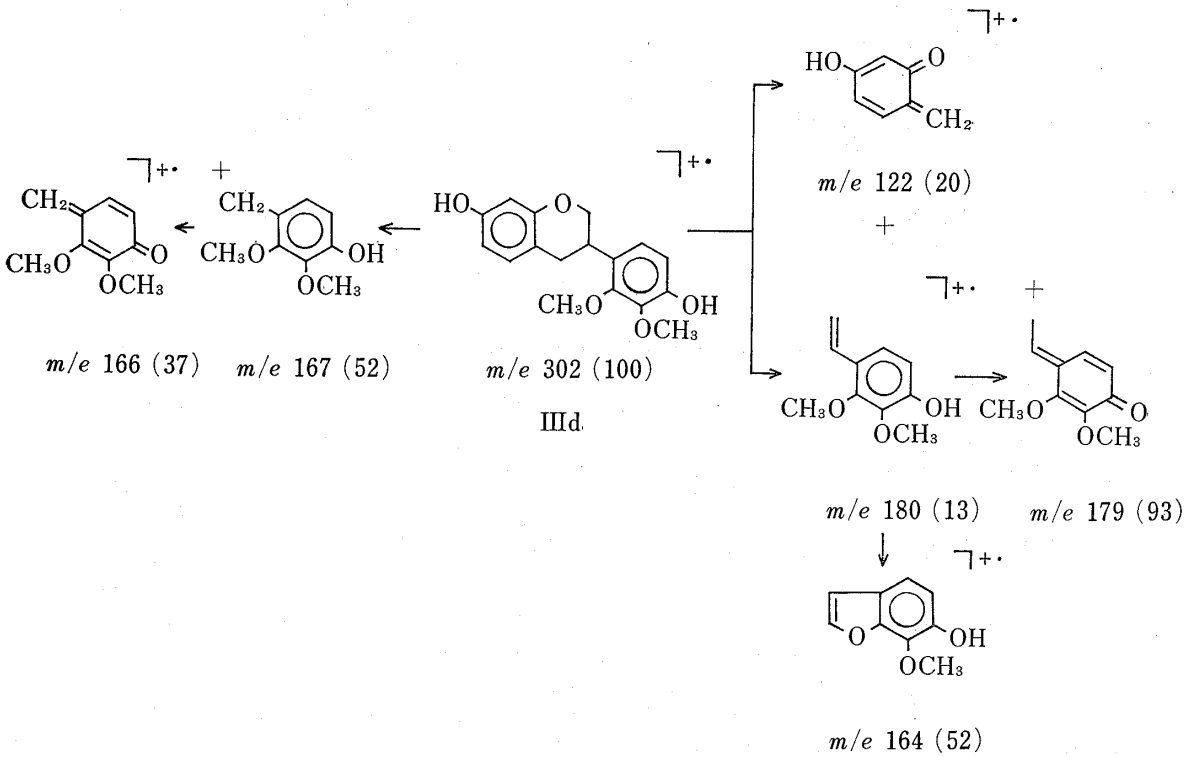


Chart 2

9) L. Jurd, *Tetrahedron Lett.*, **1976**, 1741.
10) L. Jurd and G.D. Manners, *J. Agric. Food Chem.*, **25**, 723 (1977).
11) W.D. Ollis, I.O. Sutherland, H.M. Alves, and O. Gottlieb, *Phytochemistry*, **17**, 1401 (1978).
12) A.J. Brink, G.J.H. Rall, and J.P. Engelbrecht, *Tetrahedron*, **30**, 311 (1974).
13) T. Saitoh, T. Kinoshita, and S. Shibata, *Chem. Pharm. Bull.*, **24**, 752 (1976).
14) A. Pelter and P.I. Amenechi, *J. Chem. Soc.* (*C*), **1969**, 887.

of IIIa on irradiation at the two methoxyl signals. Thus, IIIa was established as 4′,7-dihydroxy-2′,3′-dimethoxyisoflav-3-en.

Haginin B (IVa) was isolated as the diacetate (IVb), colorless needles, mp 128—129°, M^+ 354.1094 (Calcd for $C_{20}H_{18}O_6$: 354.1104), $C_{20}H_{18}O_6$. The UV spectrum of IVb showed absorption maxima at 238 sh (4.25), 287 sh (4.09) and 320 (4.25) nm (log ε). The spectrum was very similar to that of IIIb, which absorbed at 237 sh (4.34), 290 (4.18) and 320 (4.22) nm (log ε). The NMR spectrum showed the signals of two acetoxyl groups at δ 2.26 (3H, s) and δ 2.29 (3H, s), and a methoxyl group at δ 3.80 (3H, s), as well as A_2X-type proton signals at δ 5.00 (2H, d, J=1 Hz) and δ 6.56 (1H, br.s), which were characteristic of isoflav-3-en.[8–10] Two ABX-type proton signals on an aromatic ring were observed, one at δ 6.61, δ 6.62 and δ 7.03 (1H, d, J=9 Hz) on the A ring and the other at δ 6.64, δ 6.70 (1H, dd, J=8 Hz, J=2 Hz) and δ 7.27 (1H, d, J=8 Hz) on the B ring. The MS spectrum of IVc, obtained from IVb by hydrogenation over palladium-charcoal, showed prominent ion peaks at *m/e* 192 (24), 150 (100) and 135 (58) which were derived from a retro Diels-Alder fragmentation (Chart 3).[13,14] These ion peaks suggested that an acetoxyl group was attached to the A ring and an acetoxyl and a methoxyl group to the B ring. The location of the methoxyl group (C_2') was confirmed by the observation of NOE (*ca.* 20%) only at C_3'-H on irradiation at the methoxyl proton signal in IVb. Thus IVa was established as 4′,7-dihydroxy-2′-methoxyisoflav-3-en.

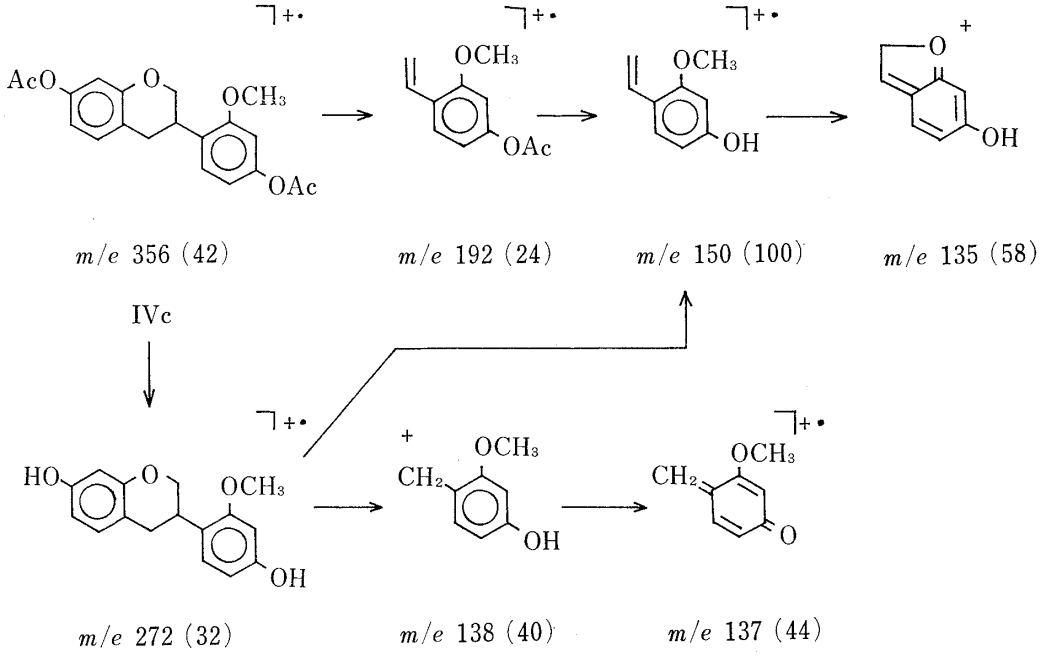


Chart 3

Experimental

Melting points were determined on a Yanaco micromelting point apparatus MP-500 and uncorrected. Optical rotation was determined with a Yanaco automatic polarimeter. IR spectra were obtained in a KBr disk or in $CHCl_3$ solution with a Jasco IRA-2 grating infrared spectrophotometer and MS spectra were recorded on Hitachi RMU-7 and JEOL JMS-01SG-2 mass spectrometer. UV spectra were obtained in methanolic solution with a Hitachi 124 spectrophotometer. ^{1}H-NMR spectra were taken at 100 MHz on a Varian HA-100 spectrometer and at 60 MHz on a Hitachi R-24B spectrometer and ^{13}C-NMR spectra were taken at 25.2 MHz on a Varian HA-100 Spectrometer; chemical shifts were given in δ (ppm) with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad). Column chromatography was carried out with Kieselgel 60 (Merck) and thin-layer chromatography was conducted on Kieselgel GF_{254} (Merck).

Extraction of Bark——Air-dried bark of *Lespedeza cyrtobotrya* Miq. (200 g) was extracted with hot methanol. The methanolic extract was concentrated *in vacuo* and the residue was partitioned between

ethyl acetate and water. The ethyl acetate-soluble fraction (7g) was chromatographed on a silica gel column using hexane–acetone as an eluent.

Xanthoangelol (II) was obtained as orange-yellow needles (700 mg). It gave a dark greenish-brown color with ferric chloride and a red color with magnesium–hydrochloric acid and with sulfuric acid. *Anal.* Calcd for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.64; H, 7.24. MS *m/e*: 392.1993 (Calcd for $C_{25}H_{28}O_4$: 392.1991). UV λ_{max}^{MeOH} nm (log ε): 228 sh (4.20), 366 (4.51). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380, 1625, 1605, 1590, 1542, 1515, 1490, 1440 NMR (acetone-d_6) δ: 1.56 (3H, s, C_8''–H_3), 1.61 (3H, s, C_9''–H_3), 1.79 (3H, s, C_{10}''–H_3), 1.89 —2.08 (4H, m, C_4''–H_2, C_5''–H_2), 3.39 (2H, d, J=7 Hz, C_1''–H_2), 5.07 (1H, m, C_6''–H), 5.30 (1H, m, C_1''–H_2), 6.55 (1H, d, J=9 Hz, C_5'–H), 6.90 (2H, d, J=8 Hz, C_3–H, C_5–H), 7.70 (2H, d, J=8 Hz, C_2–H, C_6–H), 7.74 (1H, d, J=15 Hz, C_α–H), 7.78 (1H, d, J=15 Hz, C_β–H), 7.93 (1H, d, J=9 Hz, C_6'–H), 13.94 (1H, s, OH). ^{13}C–NMR (acetone-d_6) δ: 16.3, 17.7, 22.2, 25.8, 27.3, 40.4, 108.0, 114.3, 116.1, 116.7, 118.3, 123.1, 125.1, 127.5, 130.0, 131.4, 131.5, 135.1, 144.8, 160.7, 162.6, 165.1, 192.8. This was shown to be identical with an authentic sample by direct comparison (TLC, IR).

Lespeol (I) was obtained as an orange-yellow viscous oil (370 mg). It gave a dark greenish-brown color with ferric chloride and a red color with magnesium–hydrochloric acid and with sulfuric acid. *Anal.* Calcd for $C_{25}H_{26}O_4$; C, 76.90; H, 6.71. Found: C, 76.57; H, 6.78. MS *m/e*: 390.1838 (Calcd for $C_{25}H_{26}O_4$: 390.1836). UV λ_{max}^{MeOH} nm (log ε): 229 (4.28), 280 (4.07), 371 (4.53). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3260, 1630, 1608, 1580, 1560, 1510, 1486, 1440. NMR ($CDCl_3$) δ: 1.42 (3H, s, C_{10}''–H_3), 1.56 (3H, s, C_8''–H_3), 1.65 (3H, s, C_9''–H_3), 1.72 (2H, m, C_4''–H_2), 2.06 (2H, m, C_5''–H_2), 5.08 (1H, m, C_6''–H), 5.52 (1H, d, J=10 Hz, C_1''–H), 6.35 (1H, d, J=9 Hz, C_5'–H), 6.77 (1H, d, J=10 Hz, C_1''–H), 6.84 (2H, d, J=9 Hz, C_3–H, C_5–H), 7.38 (1H, d, J=15 Hz, C_α–H), 7.50 (2H, d, J=9 Hz, C_2–H, C_6–H), 7.67 (1H, d, J=9 Hz, C_6'–H), 7.80 (1H, d, J=15 Hz, C_β–H), 13.73 (1H, s, OH). ^{13}C–NMR (acetone-d_6) δ: 17.6, 23.3, 25.8, 27.3, 42.2, 80.9, 108.6, 109.7, 114.8, 116.8, 116.9, 118.1, 124.8, 127.5, 128.0, 131.8, 132.1, 132.2, 145.4, 160.8, 161.0, 161.7, 193.1.

Oxidation of Xanthoangelol (II)——A solution of I (200 mg) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (100 mg) in dry benzene (40 ml) was refluxed for 9 hr. The reaction mixture was filtered and the filtrate was concentrated. The residue was chromatographed on silica gel using hexane–ethyl acetate (9: 1) as an eluent. I was obtained as an orange-yellow viscous oil (40 mg). This was shown to be identical with the natural product by direct comparison (TLC, IR).

Extraction of Heartwood——Air-dried heartwood of *Lespedeza cyrtobotrya* Miq. (10 kg) was extracted with hot methanol. The methanolic extract was concentrated *in vacuo* and the residue was extracted with ether and ethyl acetate successively. The ethereal extract was partitioned between hexane–benzene (1: 1) and 80% methanol. The 80% methanolic etxract (49 g) was chromatographed on silica gel using hexane–acetone as an eluent to give crude IIIa (3.5 g), IVa (240 mg), genistein (130 mg), daidzein (120 mg), dalbergioidin (5.1 g) and 3,9-dihydroxypterocarp-6a-en (190 mg). The ethyl acetate extract (35 g) was chromatographed on silica gel using hexane–acetone as an eluent to give crude isoliquiritigenin (50 mg).

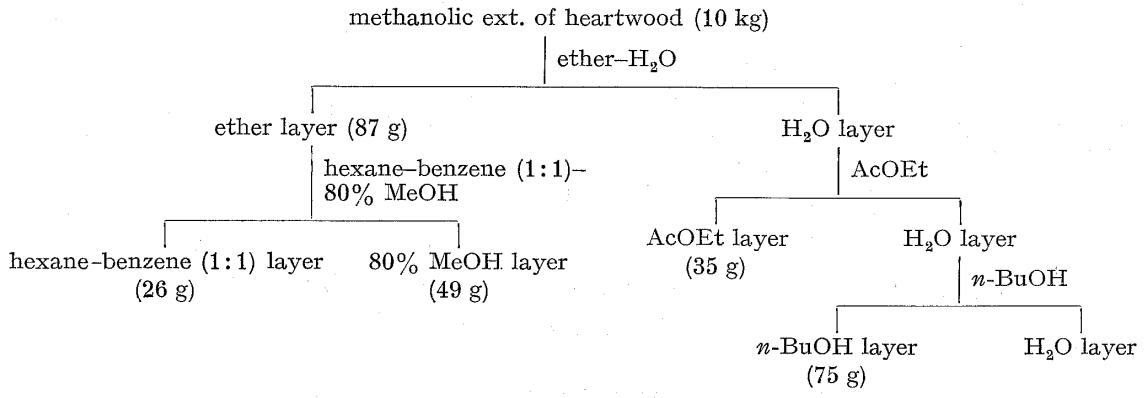


Chart 4

Genistein——Recrystallization from acetone–hexane gave colorless needles, mp 290°. This was shown to be identical with an authentic sample by direct comparison (mp, TLC, IR).

Daidzein——Recrystallization from methanol-benzene gave colorless needles, mp 325—326° (dec.). This was shown to be identical with an authentic sample by direct comparison (mp, TLC, IR).

Dalbergioidin——Recrystallization from methanol–benzene gave colorless needles, mp 234—237°. $[\alpha]_D^{25}$: 0°. This was shown to be identical with an authentic sample by direct comparison (mp, TLC).

3,9-Dihydroxypterocarp-6a-en——Recrystallization from methanol-chloroform gave slightly brown needles, mp 207—209° (dec.). *Anal.* Calcd for $C_{15}H_{10}O_4$: C, 70.87; H, 3.96. Found: C, 70.83; H, 4.14. MS *m/e*: 254 (M^+, 100). UV λ_{max}^{MeOH} nm (log ε): 228 (4.26), 239 (4.24), 247sh (4.22), 290sh (3.95), 318sh (4.33), 333 (4.56), 350 (4.51). IR ν_{max}^{KBr} cm^{-1}: 3150, 1607, 1582, 1470, 1340, 1220, 1135, 1125. NMR (acetone-d_6) δ: 5.53 (2H, s, C_5–H_2), 6.44 (1H, d, J=2 Hz, C_4–H), 6.50 (1H, dd, J=8 Hz, J=2 Hz, C_2–H), 6.82 (1H, dd, J=

8 Hz, J=2 Hz, C_8–H), 7.02 (1H, d, J=2 Hz, C_{10}–H), 7.27 (1H, d, J=8 Hz, C_7–H), 7.29 (1H, d, J=8 Hz, C_1–H). This was identified by comparison of the spectral data with those for an authentic sample.

Methylation of 3,9-Dihydroxypterocarp-6a-en——A solution of 3,9-dihydroxypterocarp-6a-en (30 mg) in methanol (2 ml) was treated with an ethereal solution of diazomethane. After standing at room temperature for 3.5 hr, the reaction mixture was concentrated and the residue was recrystallized from methanol to give dimethylether (23 mg) as colorless needles, mp 110—112° (lit. 110—112°). *Anal.* Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.26; H, 4.98. MS *m/e*: 282 (M^+, 100), 265 (M^+-CH_3, 57). UV λ_{max}^{MeOH} nm (log ε): 228 (4.23), 241 (4.21), 248sh (4.18), 290sh (3.93), 320sh(4.02), 333 (4.51), 350 (4.46). IR ν_{max}^{KBr} cm^{-1}: 1650, 1610, 1585, 1565, 1560, 1510, 1495. This was identified by comparison of the spectral data with those for an authentic sample.

Haginin A (IIIa)——Recrystallization from methanol–benzene gave colorless needles, mp 130.5—131.5°. It gave a pale yellowish-brown color with ferric chloride and a violet-brown color with diazo reagent. *Anal.* Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.17; H, 5.41. MS *m/e*: 300 (M^+, 100), 285 (M^+-CH_3, 34), 270 ($M^+-2\times CH_3$, 17). UV λ_{max}^{MeOH} nm (log ε): 237sh (4.23), 300sh (4.21), 322 (4.32). IR ν_{max}^{KBr} cm^{-1}: 3380, 1610, 1585, 1505, 1472. NMR (acetone-d_6) δ: Table I.

Acetylation of IIIa——A solution of IIIa (700 mg) in pyridine (2 ml) was treated with acetic anhydride (2 ml). After standing at room temperature for 16 hr, the reaction mixture was worked up as usual. Recrystallization from methanol gave IIIb (450 mg) as colorless prisms, mp 130—132°. *Anal.* Calcd for $C_{21}H_{20}O_7$: C, 65.61; H, 5.24. Found: C, 65.50; H, 5.29. MS *m/e*: 384 (M^+, 47), 342 (M^+-CH_2=C=O, 48), 300 ($M^+-2\times CH_2$=C=O, 100), 285 ($M^+-2\times CH_2$=C=O$-CH_3$, 27). UV λ_{max}^{MeOH} nm (log ε): 237sh (4.34), 290 (4.18), 320 (4.22). IR ν_{max}^{KBr} cm^{-1}: 1750, 1580, 1490, 1460, 1410, 1205. NMR ($CDCl_3$) δ: Table I.

Methylation of IIIa——A solution of IIIa (165 mg) in methanol (3 ml) was treated with an ethereal solution of diazomethane. After standing at room temperature for 2 days, the solvent was removed and the residue was recrystallized from hexane–acetone to give the dimethylether IIIc (84 mg) as colorless needles, mp 102—103°. *Anal.* Calcd for $C_{19}H_{20}O_5$: C, 69.52; H, 6.14. Found: C, 69.55; H, 6.14. UV λ_{max}^{MeOH} nm (log ε): 238sh (4.29), 300sh (4.23), 322 (4.34). IR ν_{max}^{KBr} cm^{-1}: 1610, 1570, 1490, 1460, 1410, 1325, 1290, 1270, 1260, 1155, 1105. This was identified by direct comparison (mp, TLC, IR) with authentic tri-O-methyl sepiol.

Hydrogenation of IIIa——IIIa (210 mg) was hydrogenated over 5% palladium–charcoal (210 mg) in methanol (5 ml). The catalyst was removed by filtration and the filtrate was concentrated to dryness *in vacuo*. The residue was recrystallized from methanol to give IIId (173 mg) as colorless needles, mp 156—157.5°. *Anal.* Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.60; H, 6.03. MS *m/e*: Chart 2. UV λ_{max}^{MeOH} nm (log ε): 280 (3.95), 288sh (3.81). IR ν_{max}^{KBr} cm^{-1}: 3450, 3330, 1600, 1500, 1465, 1220, 1170. NMR (acetone-d_6) δ: 2.80 (m, C_4–H_β), 2.83 (m, C_4–H_α), 3.43 (1H, m, C_3–H), 3.82 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 3.92 (1H, t, J=10 Hz, C_2–H_α), 4.15 (1H, m, C_2–H_β), 6.29 (1H, d, J=2 Hz, C_8–H), 6.36 (1H, dd, J=8 Hz, J=2 Hz, C_6–H), 6.63 (1H, d, J=8 Hz, C_5'–H), 6.79 (1H, d, J=8 Hz, C_6'–H), 6.87 (1H, d, J=8 Hz, C_5–H), 7.95 (2H, br.s, OH).

Acetylation of Crude IVa——A solution of crude IVa (240 mg) in pyridine (2 ml) was treated with acetic anhydride (2 ml). After standing at room temperature overnight, the reaction mixture was worked up as usual and purified by preparative layer chromatography using chloroform as a developer. Recrystallization from chloroform–methanol gave the diacetate (IVb) (145 mg) as colorless needles, mp 128—129°. MS *m/e*: 354.1094 (Calcd for $C_{20}H_{18}O_6$: 354.1104), 312.1068 (Calcd for $C_{18}H_{16}O_5$: 312.1000), 270.0905 (Calcd for $C_{16}H_{14}O_4$: 270.0893). UV λ_{max}^{MeOH} nm (log ε): 238sh (4.25), 287sh (4.09), 320 (4.25). IR ν_{max}^{KBr} cm^{-1}: 1760, 1605, 1500, 1225, 1210, 1145. NMR ($CDCl_3$) δ: 2.26, 2.29 (each 3H, s, $OCOCH_3$), 3.80 (3H, s, OCH_3), 5.00 (2H, d, J=1 Hz, C_2–H_2), 6.56 (1H, br.s, C_4–H), 6.61 (br.s, C_8–H), 6.62 (C_6–H), 6.64 (br.s, C_3'–H), 6.70 (1H, dd, J=8 Hz, J=2 Hz, C_5'–H), 7.03 (1H, d, J=9 Hz, C_5–H), 7.27 (1H, d, J=8 Hz, C_6'–H).

Hydrogenation of IVb——IVb (20 mg) was hydrogenated over 5% palladium–charcoal (30 mg) in benzene (2 ml). The catalyst was removed by filtration and the filtrate was concentrated to dryness *in vacuo*. The residue was recrystallized from methanol to give IVc (10 mg) as colorless needles, mp 101—102.5°. MS *m/e*: Chart 3. IR ν_{max}^{KBr} cm^{-1}: 1750, 1608, 1590, 1500, 1215, 1147.

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