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Studies on the Pterocarpans from *Melilotus alba* Desr.

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Five new pterocarpans, melilotocarpans A (I), B (II), C (III), D (IV) and E (V), have been isolated from *Melilotus alba* Desr. and their structures have been determined from chemical and spectral data.

Keywords——*Melilotus alba*; Leguminosae; pterocarpans; melilotocarpan A; melilotocarpan B; melilotocarpan C; melilotocarpan D; melilotocarpan E

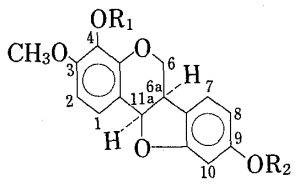
As part of our studies on isoflavonoids from Leguminosae pants, we now report the isolation and structure elucidation of five new pterocarpans, melilotocarpans A, B, C, D and E, from *Melilotus alba* Desr. All of these compounds showed a positive diazo reaction and gave a phenolic acetate, a phenolic methyl ether (both in the usual way) and an isoflavan upon hydrogenation. The nuclear magnetic resonance (NMR) spectra of these five compounds showed methoxyl group(s), aromatic protons and ABMX-type proton signals which are characteristic of pterocarpan (H-6_{ax}, H-6_a, H-6_{eq} and H-11_a, respectively)[1] (Table I).

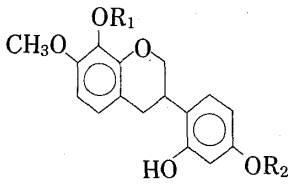
Melilotocarpan A (I), $C_{17}H_{16}O_5$, M+ 300.1020 (Calcd for $C_{17}H_{16}O_5$ 300.1000), mp 48—51°C, $[\alpha]_D^{23}$ −194°. The infrared (IR) spectrum suggested the presence of a hydroxyl group (3470 cm^{-1}) and aromatic rings (1618, 1580, 1495, 1470, 1442 cm^{-1}). The ultraviolet (UV) spectrum showed absorption maxima at 283 (3.79) and 289 (sh 3.67) nm (log ε). The NMR spectrum showed two methoxyl groups (δ 3.78 and 3.92) and five aromatic protons as AB-type signals (δ 6.68 and 7.06, J=9 Hz) and ABX-type signals [δ 6.43 (J=2 Hz), 6.45 (J=9 and 2 Hz) and 7.14 (J=9 Hz)]. Nuclear Overhauser effect (NOE) was observed at the proton signals [δ 6.68 (*ca.* 14%)] and [δ 6.43 and 6.45 (total *ca.* 10%)] on irradiation at the methoxyl groups (δ 3.78) and (δ 3.92), respectively. The mass spectrum (MS) of Ia, obtained from I by hydrogenation over palladium-charcoal, showed prominent ions VI, VII and VIII at m/z 153 (41), 150 (89) and 137 (100), respectively, which were due to retro Diels–Alder fragmentation (Chart 2). These ions suggested that a hydroxyl group and a methoxyl group are attached to the A ring and a methoxyl group to the B ring of I.

Methylation of I with dimethylsulfate and potassium carbonate in acetone afforded 3,4,9-trimethoxypterocarpan (Ib), mp 120—122°C, which had already been isolated from *Swartzia madagascariensis*.[2]

Acetylation of I with acetic anhydride in pyridine afforded the monoacetate (Ic), mp 161—162°C. In the NMR spectrum of Ic, a proton signal assigned to H-1 showed a downfield shift (0.33 ppm). Thus, the structure of I was established as 3,9-dimethoxy-4-hydroxypterocapan.

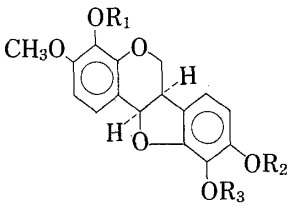
Melilotocarpan B (II), $C_{16}H_{14}O_5$, M+ 286.0863 (Calcd for $C_{16}H_{14}O_5$ 286.0844), mp 173—175.5°C, $[\alpha]_D^{23}$ −179°. The IR spectrum suggested the presence of hydroxyl groups (3500, 3300 cm^{-1}) and aromatic rings (1620, 1510, 1495, 1475, 1455 cm^{-1}). The UV spectrum showed absorption maxima at 283 (3.77) and 291 (sh 3.65) nm (log ε). The NMR spectrum showed a methoxyl group (δ 3.84) and five aromatic protons as AB-type signals (δ 6.72 and 6.96, J=9 Hz) and as ABX-type signals [δ 6.31 (J=2 Hz), 6.37 (J=9 and 2 Hz) and 7.13 (J=9 Hz)]. On irradiation at the methoxyl signal (δ 3.84), NOE (*ca.* 12%) was observed at the proton signal (δ 6.72). These spectral data are very similar to those of I, except that II has only one methoxyl group.

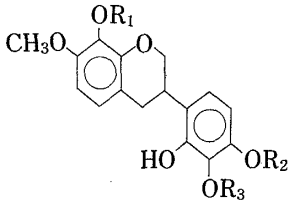




I: $R_1=H$, $R_2=CH_3$
Ib (=IIb): $R_1=CH_3$, $R_2=CH_3$
Ic: $R_1=COCH_3$, $R_2=CH_3$
II: $R_1=H$, $R_2=H$
IIc: $R_1=COCH_3$, $R_2=COCH_3$

Ia: $R_1=H$, $R_2=CH_3$
IIa: $R_1=H$, $R_2=H$





III: $R_1=H$, $R_2=CH_3$, $R_3=CH_3$
IIIb (=IVb=Vb): $R_1=CH_3$, $R_2=CH_3$, $R_3=CH_3$
IIIc: $R_1=COCH_3$, $R_2=CH_3$, $R_3=CH_3$
IV: $R_1=H$, $R_2=CH_3$, $R_3=H$
IVc: $R_1=COCH_3$, $R_2=CH_3$, $R_3=COCH_3$
V: $R_1=H$, $R_2=H$, $R_3=CH_3$
Vc: $R_1=COCH_3$, $R_2=COCH_3$, $R_3=CH_3$

IIIa: $R_1=H$, $R_2=CH_3$, $R_3=CH_3$
IVa: $R_1=H$, $R_2=CH_3$, $R_3=H$
Va: $R_1=H$, $R_2=H$, $R_3=CH_3$

Chart 1

TABLE I. NMR Chemical Shifts and Coupling Constants

Proton	I	II	III	IV	V
1	7.06 (d, J=9 Hz)	6.96 (d, J=9 Hz)	7.11 (d, J=9 Hz)	7.13 (d, J=9 Hz)	7.08 (d, J=8 Hz)
2	6.68 (d, J=9 Hz)	6.72 (d, J=9 Hz)	6.65 (d, J=9 Hz)	6.66 (d, J=9 Hz)	6.67 (d, J=8 Hz)
7	7.14 (d, J=9 Hz)	7.13 (d, J=9 Hz)	6.89 (d, J=8 Hz)	6.75 (d, J=8 Hz)	6.82 (d, J=8 Hz)
8	6.45 (dd, J=9 Hz, J=2 Hz)	6.37 (dd, J=9 Hz, J=2 Hz)	6.46 (d, J=8 Hz)	6.45 (d, J=8 Hz)	6.50 (d, J=8 Hz)
10	6.43 (d, J=2 Hz)	6.31 (d, J=2 Hz)			
$6_a, 6_{ax}$	3.4—3.7 (m)	3.4—3.8 (m)	3.4—3.8 (m)	3.4—3.8 (m)	3.4—3.8 (m)
6_{eq}	4.34 (m)	4.31 (m)	4.34 (m)	4.25 (m)	4.35 (m)
11_a	5.53 (d, J=6 Hz)	5.53 (d, J=6 Hz)	5.55 (d, J=6 Hz)	5.59 (d, J=6 Hz)	5.64 (d, J=6 Hz)
OCH_3	3.78 (s) 3.92 (s)	3.84 (s)	3.84 (s) 3.90 (s) 3.93	3.88 (s) 3.92 (s)	3.91 (s) 3.99 (s)

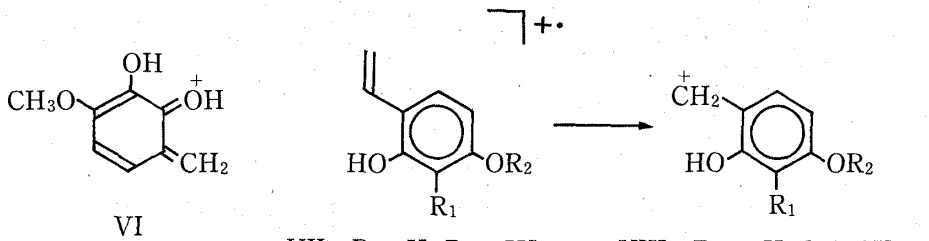
The MS of IIa, obtained from II by hydrogenation, showed prominent ions VI, IX and X at m/z 153 (97), 136 (60) and 123 (100), respectively (Chart 2). These ions suggested that a hydroxyl group and a methoxyl group were attached to the A ring and a hydroxyl group to the B ring of II.

Methylation of II afforded the 3,4,9-trimethoxypterocarpan (IIb).

Acetylation of II afforded the diacetate (IIc), mp 183—185°C. In the NMR spectrum of IIc, three proton signals assigned to H-1, H-8 and H-10, showed downfield shifts (0.42, 0.26 and 0.27 ppm, respectively).

Thus, the structure of II was established as 4,9-dihydroxy-3-methoxypterocarpan.

Melilotocarpan C (III), $C_{18}H_{18}O_6$, mp 160—162.5°C, $[\alpha]_D^{18}$ −219°. The IR spectrum suggested the presence of a hydroxyl group (3430 cm^{-1}) and aromatic rings (1620, 1580, 1490,



VI

VII : R_1=H, R_2=CH_3 VIII : R_1 =H, R_2=CH_3
IX : R_1=H, R_2=H X : R_1=H, R_2=H
XI : R_1=OCH_3, R_2=CH_3 XII : R_1=OCH_3, R_2=CH_3
XIII : R_1=OH, R_2=CH_3 XIV : R_1=OH, R_2=CH_3
XV : R_1=OCH_3, R_2=H XVI : R_1=OCH_3, R_2=H

Chart 2

1450 cm^{-1}). The UV spectrum showed absorption maxima at 274 (3.49) and 281 (sh 3.47) nm (log ε). The NMR spectrum showed three methoxyl groups (δ 3.84, 3.90, 3.93) and two pairs of AB-type proton signals [δ 6.46, 6.89 (J=8 Hz) and δ 6.65, 7.11 (J=9 Hz)]. On irradiation at the methoxyl signals (δ 3.84 and 3.90), NOE was observed at the proton signals at δ 6.48 (*ca.* 15%) and δ 6.65 (*ca.* 18%).

The MS of the reduction product IIIa showed prominent ions VI, XI and XII at *m/z* 153 (41), 180 (78) and 167 (100), respectively (Chart 2), indicating the presence of a hydroxyl group and a methoxyl group on the A ring and two methoxyl groups on the B ring of III.

Methylation of III afforded the methyl ether (IIIb), mp 189—201°C.

Acetylation of III afforded the monoacetate (IIIc), mp 162—163°C. In the NMR spectrum of IIIc, the proton signal assigned to H-1 showed a downfield shift (0.34 ppm). From these data, the structure of III was established as 4-hydroxy-3,9,10-trimethoxypterocarpan.

Melilotocarpan D (IV), $C_{17}H_{16}O_6$, mp 161—162.5°C, $[\alpha]_D^{23}$ −210°. The IR spectrum suggested the presence of hydroxyl groups (3500, 3350 cm^{-1}) and aromatic rings (1620, 1580, 1495, 1470 cm^{-1}). The UV spectrum is similar to that of III, showing absorption maxima at 271 (3.41) and 281 (sh 3.21) nm (log ε). The NMR spectrum is also similar to that of III, except that IV has two methoxyl groups. On irradiation at the methoxyl signals (δ 3.88 and 3.92), NOE was observed at the proton signals at δ 6.45 (*ca.* 14%) and δ 6.66 (*ca.* 15%).

The reduction product IVa rapidly reduced ammoniac silver nitrate. Therefore, the B ring has an *ortho*-dihydroxyl group.

The MS of IVa showed prominent ions VI (and XIV) and XIII at *m/z* 153 (100) and 166 (27), respectively (Chart 2). Therefore both the A ring and the B ring of IV have a hydroxyl and a methoxyl group.

Methylation of IV afforded the methyl ether (IVb), mp 189—190.5°C, which was identical with IIIb.

Acetylation of IV afforded the diacetate (IVc). In the NMR spectrum of IVc, two proton signals assigned to H-1 and H-7 showed downfield shifts (0.28 and 0.29 ppm, respectively). Thus, the structure of IV was established as 4,10-dihydroxy-3,9-dimethoxypterocarpan.

Melilotocarpan E (V), $C_{17}H_{16}O_6$, mp 197—199°C, $[\alpha]_D^{22}$ −169°. The IR spectrum suggested the presence of hydroxyl groups (3500 cm^{-1}) and aromatic rings (1620, 1600, 1500, 1490, 1460, 1445 cm^{-1}). The UV spectrum showed absorption maxima at 275 (3.52) and 282 (sh 3.49) nm (log ε), which were similar to those of III and IV. The NMR spectrum showed two methoxyl groups (δ 3.91, 3.99) and two pairs of AB-type proton signals [δ 6.67, 7.08 (J= 8 Hz) and δ 6.50, 6.82 (J=8 Hz)]. On irradiation at the methoxyl signal (δ 3.91), NOE (*ca.* 21%) was observed at the proton signal (δ 6.67) assigned to H-2, but the irradiation at δ 3.99 did not influence the latter signal.

The MS of the reduction product Va showed prominent ions VI (and XVI) and XV at *m/z* 153 (100) and 166 (36), respectively (Chart 2). which were very similar to those of IVa. Therefore both the A ring and the B ring of V have a hydroxyl group and a methoxyl group.

Methylation of V afforded the methyl ether (Vb), mp 189—190.5°C, which was identical with IIIb.

Acetylation of V afforded the diacetate (Vc), mp 163—164.5°C. In the NMR spectrum of Vc, the proton signal assigned to H-1 showed a downfield shift (0.33 ppm). From these data the structure of V was established as 4,9-dihydroxy-3,10-dimethoxypterocarpan.

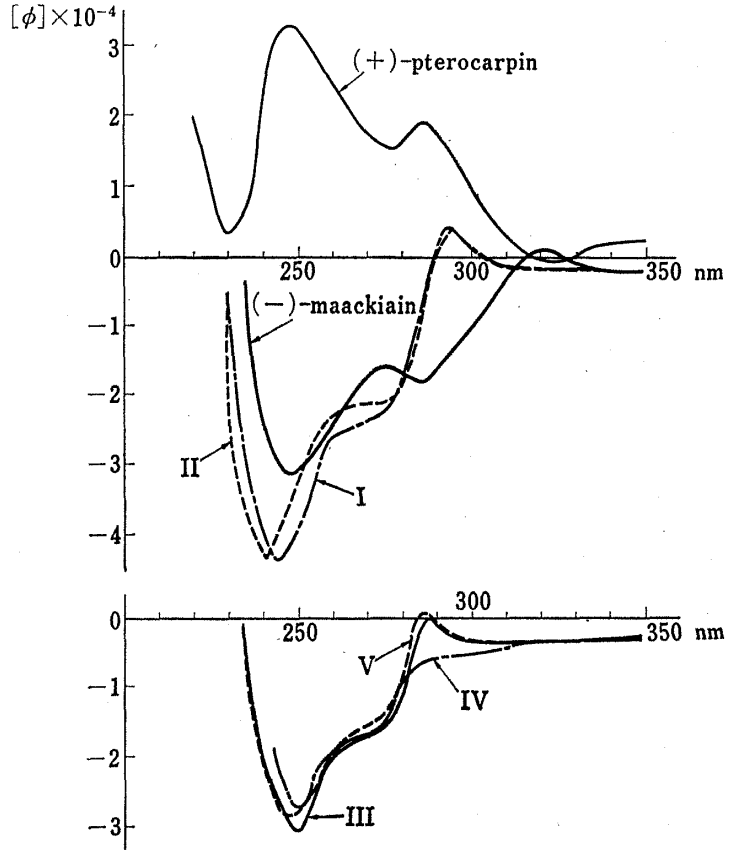


Fig. 1. ORD Curves of (+)-Pterocarpin, (−)-Maackiain, I, II, III, IV and V in Methanol

The optical rotatory dispersion (ORD) curves of the five (−)-pterocarpans, I, II, III, IV, V, are characterized by similar multiple Cotton effects in the 240—330 nm region; they are approximately mirror images of the curve showed by (+)-pterocarpin and are similar to that of (−)-maackiain (Fig. 1). Therefore we deduced the 6a*R*, 11a*R*-configuration for the five pterocarpans.[3)]

Experimental

Melting points were determined on a Yanaco MP-500 micro melting point apparatus and are uncorrected. Optical rotations were determined with a Yanaco automatic polarimeter. IR spectra were run on a JASCO IRA-2 grating infrared spectrophotometer, UV spectra on a Hitachi 124 spectrophotometer and MS on a Hitachi RMU-7 or a JEOL 01SG-2 mass spectrometer. NMR spectra were recorded on a JEOL FX-90Q spectrometer; chemical shifts are given in δ (ppm) with tetramethylsilane as an internal standard (s, singlet; d, doublet; m, multiplet). ORD spectra were run on a JASCO ORD/UV-5 optical rotatory dispersion recorder.

Isolation——Air-dried *Melilotus alba* (aerial part; 4.3 kg) was extracted twice with hot methanol (25 l). The methanolic extract was concentrated *in vacuo* and the residue was extracted with ethyl acetate and

n-butanol successively. The ethyl acetate extract (100 g) was chromatographed on silica gel (1 kg) using hexane–acetone as an eluent to give seven fractions. After repeated column chromatography of these fractions on silica gel and/or polyamide, melilotocarpans A (I) (72 mg), B (II) (347 mg), C (III) (193 mg), D (IV) (27 mg), E (V) (650 mg) were isolated.

Melilotocarpan A (I)——Recrystallization from methanol gave colorless needles, mp 48—51°C, $[\alpha]_D^{23}$ −194° (c=1.40, dioxane). This material gave an orange color with the diazo reagent. MS *m/z*: 300.1020 (Calcd for $C_{17}H_{16}O_5$: 300.1000). IR ν_{max}^{KBr} cm^{-1}: 3470, 1618, 1590, 1495, 1470, 1442, 1280, 1218, 1142, 1095. UV λ_{max}^{MeOH} nm (log ε): 283 (3.79), 298 (sh 3.67). NMR ($CDCl_3$) δ: Table I. ORD (c=0.0058, methanol): Fig. 1.

Hydrogenation of I——I (35 mg) was hydrogenated over 5% palladium-charcoal (50 mg) in acetic acid (10 ml) at 70°C. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was purified by thin-layer chromatography using benzene-methanol (9: 1) as a developer to give a colorless powder (20 mg). MS *m/z*: 302 (M^+, 53), 153 (41), 150 (89), 137 (100). IR ν_{max}^{KBr} cm^{-1}: 3450, 1610, 1585, 1510, 1490, 1285, 1200, 1155, 1100.

Methylation of I——A solution of I (11 mg) in dry acetone (1.5 ml) containing anhydrous potassium carbonate (30 mg), was treated with five drops of dimethyl sulfate. The reaction mixture was refluxed for 2 h, filtered and concentrated. The residue was purified by thin-layer chromatography using hexane–ethyl acetate (6: 4) to give the methyl ether (Ib) (7 mg), mp 120—122°C, as colorless needles from methanol. MS *m/z*: 314 (M^+, 100), 299 (M^+-CH_3, 30). IR ν_{max}^{KBr} cm^{-1}: 1610, 1500, 1470, 1450, 1290, 1280, 1230, 1190, 1170, 1150, 1110. NMR ($CDCl_3$) δ: 3.4—3.8 (2H, m, H-6$_{ax}$, H-6$_a$), 3.78, 3.87, 3.90 (each 3H, s, OCH_3), 4.4 (1H, m, H-6$_{eq}$), 5.51 (1H, d, J=6 Hz, H-11$_a$), 6.45 (2H, m, H-8, H-10), 6.67 (1H, d, J=9 Hz, H-2), 7.13 (1H, d, J=9 Hz, H-7), 7.24 (1H, d, J=9 Hz, H-1). This compound was concluded to be 3,4,9-trimethoxypterocarpan by data comparison (mp, NMR) with literature values.[2]

Acetylation of I——I (22 mg) was dissolved in pyridine (0.3 ml) and acetic anhydride (0.3 ml) and the solution was left at room temperature overnight. The solution was concentrated *in vacuo* and the residue was purified by thin-layer chromatography using hexane–ethyl acetate (6: 4) as a developer. Recrystallization from methanol gave the monoacetate (Ic) (14 mg) as colorless needles, mp 161—162°C. MS *m/z*: 342 (M^+, 44), 300 (M^+-CH_2=C=O, 100), 285 (M^+-CH_2=C=O $-CH_3$, 33). IR ν_{max}^{KBr} cm^{-1}: 1760, 1625, 1595, 1495, 1475, 1445, 1295, 1285, 1195, 1150, 1110. NMR ($CDCl_3$) δ: 3.4—3.7 (2H, m, H-6$_{ax}$, H-6$_a$), 3.77, 3.85 (each 3H, s, OCH_3), 4.29 (1H, m, H-6$_{eq}$), 5.53 (1H, d, J=6 Hz, H-11$_a$), 6.45 (1H, d, J=2 Hz, H-10), 6.45 (1H, dd, J=9 Hz, J=2 Hz, H-8), 6.72 (1H, d, J=8 Hz, H-2), 7.13 (1H, d, J=9 Hz, H-7), 7.39 (1H, d, J=8 Hz, H-1).

Melilotocarpan B (II)——Recrystallization from chloroform–methanol gave colorless prisms, mp 173—175.5°C, $[\alpha]_D^{23}$ −179° (c=2.17, dioxane). This material gave an orange color with the diazo reagent. MS *m/z*: 286.0863 (Calcd for $C_{16}H_{14}O_5$: 286.0844). IR ν_{max}^{KBr} cm^{-1} 3500, 3300, 1620, 1510, 1495, 1475, 1455, 1380, 1290, 1220, 1140, 1100, 1020. UV λ_{max}^{MeOH} nm (log ε): 283 (3.77), 291 (sh 3.65). NMR (acetone-d_6) δ: Table I. ORD (c=0.0052, methanol): Fig. 1.

Hydrogenation of II——II (51 mg) was hydrogenated in the same way as I. The reaction product was purified by silica gel column chromatography using benzene–methanol (94: 6) as an eluent to give a colorless powder (11.5 mg). MS *m/z*: 288 (M^+, 77), 153 (97), 136 (60), 123 (100). IR ν_{max}^{KBr} cm^{-1}: 3400, 1620, 1605, 1510, 1500, 1460, 1450, 1360, 1290, 1250, 1210, 1160, 1100.

Methylation of II——Substance II (30 mg) was methylated in the same was as I to give the methyl ether (IIb) (20 mg), mp 122—123.5°C, as colorless plates (from methanol). MS *m/z*: 314 (M^+, 100), 299 (M^+-CH_3, 23). IR ν_{max}^{KBr} cm^{-1}: 1610, 1500, 1470, 1450, 1290, 1280, 1230, 1190, 1170, 1150, 1110. This product was identified by direct comparison (mp, IR, MS, TLC) with the methyl ether (Ib) of melilotocarpan A.

Acetylation of II——II (49 mg) was acetylated in the usual way with pyridine and acetic anhydride to give the diacetate (IIc) (52 mg) as colorless prisms (from methanol), mp 183—185°C. MS *m/z*: 370 (M^+, 7), 328 (M^+-CH_2=C=O, 59), 286 ($M^+-2\times CH_2$=C=O, 100). IR ν_{max}^{KBr} cm^{-1}: 1770, 1630, 1515, 1490, 1480, 1390, 1300, 1200, 1110. NMR ($CDCl_3$) δ: 2.26, 2.33 (each 3H, s, $OCOCH_3$), 3.4—3.7 (2H, m, H-6$_{ax}$, H-6$_a$), 3.84 (3H, s, OCH_3), 4.30 (1H, m, H-6$_{eq}$), 5.56 (1H, d, J=6 Hz, H-11$_a$), 6.58 (1H, d, J=2 Hz, H-10), 6.63 (1H, dd, J=9 Hz, J=2 Hz, H-8), 6.72 (1H, d, J=8 Hz, H-2), 7.20 (1H, d, J=9 Hz, H-7), 7.38 (1H, d, J=8 Hz, H-1).

Melilotocarpan C (III)——Recrystallization from acetone gave colorless needles, mp 160—162.5°C, $[\alpha]_D^{18}$ −219° (c=1.40, dioxane). This material gave an orange color with the diazo reagent. *Anal.* Calcd for $C_{18}H_{18}O_6$: C, 65.44; H, 5.49. Found: C, 65.38; H, 5.54. MS *m/z*: 330 (M^+, 100), 315 (M^+-CH_3, 44). IR ν_{max}^{KBr} cm^{-1}: 3430, 1620, 1580, 1490, 1450, 1290, 1270, 1090. UV λ_{max}^{MeOH} nm (log ε): 274 (3.49), 281 (sh 3.47). NMR ($CDCl_3$) δ: Table I. ORD (c=0.0066, methanol): Fig. 1.

Hydrogenation of III——III (40 mg) was hydrogenated in the same way as above. Purification of the reaction product by silica gel column chromatography using benzene–methanol (96: 4) as an eluent gave the isoflavan (IIIa) (22 mg) as colorless needles (from methanol), mp 160—161°C. MS *m/z*: 332 (M^+, 59), 180 (78), 167 (100), 153 (41). IR ν_{max}^{KBr} cm^{-1}: 3450, 3380, 1630, 1620, 1515, 1485, 1475, 1465, 1450, 1435, 1220, 1115, 1105.

Methylation of III—III (53 mg) was treated with an ethereal solution of diazomethane. After standing at room temperature for 4 h, the reaction mixture was concentrated and the residue was purified by thin-layer chromatography using hexane–ethyl acetate (6: 4) as a developer to give the methyl ether (IIIb) (33 mg) as colorless needles (from chloroform–methanol), mp 189—191.5°C, MS *m/z*: 344 (M^+, 100), 329 (M^+-CH_3,

44), 191 (35), 178 (15). IR ν_{max}^{KBr} cm^{-1}: 1615, 1500, 1480, 1465, 1450, 1295, 1275, 1115, 1090.

Acetylation of III——III (94 mg) was acetylated in the same way as above to give the monoacetate (IIIc) (78 mg) as colorless plates (from methanol), mp 162—163°C. *Anal.* Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.51; H, 5.45. MS *m/z*: 327 (M^+, 79), 330 (M^+-CH_2=C=O, 100), 315 (M^+-CH_2=C=O $-CH_3$, 51). IR ν_{max}^{KBr} cm^{-1}: 1760, 1620, 1500, 1465, 1455, 1290, 1275, 1230, 1190, 1170, 1110, 1090. NMR ($CDCl_3$) δ: 2.35 (3H, s, $OCOCH_3$), 3.4—3.8 (2H, m, H-6_{ax}, H-6_a), 3.85, 3.95 (each 3H, s, OCH_3), 4.30 (1H, m, H-6_{eq}), 5.55 (1H, d, J=6 Hz, H-11_a), 6.46 (1H, d, J=8 Hz, H-8), 6.71 (1H, d, J=9 Hz, H-2), 6.87 (1H, d, J=8 Hz, H-7), 7.45 (1H, d, J=9 Hz, H-1).

Melilotocarpan D (IV)——Recrystallization from methanol gave colorless needles, mp 161—162.5°C, $[\alpha]_D^{23}$ −210° (c=1.00, dioxane). This material gave an orange color with the diazo reagent. *Anal.* Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10. Found: C, 64.32; H, 5.10. MS *m/z*: 316 (M^+, 100), 301 ($M^+ -CH_3$, 56). IR ν_{max}^{KBr} cm^{-1}: ~3500, 3350, 1620, 1580, 1495, 1470, 1280, 1260, 1250, 1080. UV λ_{max}^{MeOH} nm (log ε): 271 (3.41), 281 (sh 3.21). NMR ($CDCl_3$) δ: Table I. ORD (c=0.0062, methanol): Fig. 1.

Hydrogenation of IV——IV (12 mg) was hydrogenated in the same way as above. Purification of the reaction product by silica gel column chromatography using benzene–methanol (97: 3) as an eluent gave a white powder (4.5 mg). MS *m/z*: 318 (M^+, 32), 166 (27), 153 (100). IR ν_{max}^{KBr} cm^{-1}: 3550, 3450, 3280, 1630, 1515, 1485, 1460, 1300, 1230, 1110.

Methylation of IV——IV (5 mg) was methylated with diazomethane to give the methyl ether (IVb) (4 mg) as colorless needles (from methanol), mp 189—190.5°C. MS *m/z*: 344 (M^+, 100), 329 (M^+-CH_3, 49), 191 (9), 178 (16). IR ν_{max}^{KBr} cm^{-1}: 1615, 1500, 1480, 1465, 1450, 1295, 1275, 1115, 1090. This product was identified by direct comparison (mp, IR, MS, TLC) with the methyl ether (IIIb) of melilotocarpan C.

Acetylation of IV——IV (14 mg) was acetylated in the same way as in the case of I to give the diacetate (IVc) (10 mg) as a white powder. MS *m/z*: 400 (M^+, <1), 358 (M^+-CH_2=C=O, 100), 301 (M^+-CH_2=C=O $-CH_3$, 56). IR ν_{max}^{KBr} cm^{-1}: 3450, 1760, 1630, 1500, 1475, 1370, 1190, 1090. NMR ($CDCl_3$) δ: 2.32, 2.33 (each 3H, s, $OCOCH_3$), 3.4—3.8 (2H, m, H-6_{ax}, H-6_a), 3.81, 3.85 (each 3H, s, OCH_3), 4.26 (1H, m, H-6_{eq}), 5.58 (1H, d, J=6 Hz, H-11_a), 6.50 (1H, d, J=8 Hz, H-8), 6.72 (1H, d, J=9 Hz, H-2), 7.04 (1H, d, J=8 Hz, H-7), 7.41 (1H, d, J=9 Hz, H-1).

Melilotocarpan E (V)——Recrystallization from chloroform–methanol gave colorless needles, mp 197—199°C, $[\alpha]_D^{22}$ −169° (c=3.51, dioxane). This material gave an orange color with the diazo reagent. *Anal.* Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10. Found: C, 64.56; H, 5.05. MS *m/z*: 316 (M^+, 100), 301 (M^+-CH_3, 31). IR ν_{max}^{KBr} cm^{-1}: 3500, 1620, 1600, 1500, 1490, 1460, 1445, 1290, 1220, 1190, 1170, 1110, 1100. UV λ_{max}^{MeOH} nm (log ε): 275 (3.52), 282 (sh 3.49). NMR ($CDCl_3$) δ: Table I. ORD (c=0.0055, methanol): Fig. 1.

Hydrogenation of V——V (55 mg) was hydrogenated in the same way as I. Purification of the reaction product by silica gel column chromatography using benzene–methanol (95: 5) as an eluent gave the isoflavan (Va) (34 mg) as colorless prisms (from benzene–methanol), mp 191.5—192°C. MS *m/z*: 318 (M^+, 53), 166 (36), 153 (100). IR ν_{max}^{KBr} cm^{-1}: 3450, 3375, 1625, 1510, 1470, 1360, 1330, 1300, 1200, 1105. UV λ_{max}^{MeOH} nm (log ε): 270 (3.31), 278 (sh 3.26).

Methylation of V——V (12 mg) was methylated in the same way as I. Purification of the reaction product by thin-layer chromatography using hexane–ethyl acetate (6: 4) as a developer gave the methyl ether (Vb) (10 mg) as colorless needles (from methanol), mp 189—190.5°C. MS *m/z*: 344 (M^+ 100), 329 (M^+-CH_3, 44), 191 (8), 178 (14). IR ν_{max}^{KBr} cm^{-1}: 1615, 1500, 1480, 1465, 1450, 1295, 1275, 1115, 1090. This product was identified by direct comparison (mp, IR, MS, TLC) with the methyl ether (IIIb) of melilotocarpan C.

Acetylation of V——V (86 mg) was acetylated in the same way as I. Purification of the reaction product by thin-layer chromatography using hexane–acetone (2: 1) as a developer gave the diacetate (Vc) (80 mg) as colorless plates (from methanol), mp 163—164.5°C. *Anal.* Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 62.82; H, 5.05. MS *m/z*: 400 (M^+, 36), 358 (M^+-CH_2=C=O, 50), 316 ($M^+-2\times CH_2$=C=O, 100), 301 ($M^+-2\times CH_2$=C=O$-CH_3$, 20). IR ν_{max}^{KBr} cm^{-1}: 1770, 1625, 1510, 1490, 1475, 1455, 1375, 1295, 1230, 1210, 1190, 1115. NMR ($CDCl_3$) δ: 2.30, 2.34 (each 3H, s, $OCOCH_3$), 3.4—3.8 (2H, m, H-6_{ax}, H-6_a), 3.85, 3.93 (each 3H, s, OCH_3), 4.30 (1H, m, H-6_{eq}), 5.59 (1H, d, J=6 Hz, H-11_a), 6.58 (1H, d, J=8 Hz, H-8), 6.72 (1H, d, J=9 Hz, H-2), 6.89 (1H, d, J=8 Hz, H-7), 7.41 (1H, d, J=9 Hz, H-1).

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