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# Studies on the Constituents of the Leaves of *Cassia torosa* CAV. I.[1] The Structures of Two New *C*-Glycosylflavones

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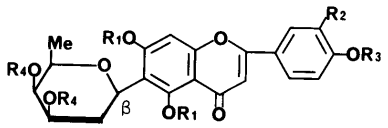
**Two novel *C*-2,6-dideoxyglycosylflavones, torosaflavones A (1) and B (2), were isolated from the leaves of *Cassia torosa* CAV. The structures of the new compounds 1 and 2 were established as apigenin 6-*C*-β-D-olioside and diosmetin 6-*C*-β-D-olioside, respectively, on the basis of spectral and X-ray analysis.**

**Keywords** *Cassia torosa*; Leguminosae; *C*-glycosylflavone; oliose; 2,6-dideoxyglycoside; torosaflavone A; torosaflavone B; 2D-NMR; CD; X-ray analysis

In previous papers,[2-9] we reported the isolation of anthraquinones, an anthrone, a dimeric anthrone, hydroanthracenes, dimeric hydroanthracenes, naphthalenic lactones, and sterols from the ripe and unripe seeds, seedlings, and roots of *Cassia torosa* CAV.

The fresh leaves of this plant are applied to the treatment of insect bites in Japan. In this paper, we wish to report the isolation and structural determination of two new *C*-glycosylflavones linked with 2,6-dideoxysugar, torosaflavones A (**1**) and B (**2**). These compounds were obtained from the ether-soluble fraction of the methanolic extract of the leaves as described in Experimental.




**1**: $R_1=R_2=R_3=R_4=H$
**2**: $R_1=R_4=H$, $R_2=OH$, $R_3=Me$
**2a**: $R_1=R_3=Me$, $R_2=OMe$, $R_4=H$
**2b**: $R_1=R_4=Ac$, $R_2=OAc$, $R_3=Me$
**2c**: $R_1=R_3=Me$, $R_2=OMe$, $R_4=Bz$

Chart 1

Compound **2**, yellow prisms, mp 240—241 °C, $C_{22}H_{22}O_9$ ($M^+$ 430.1236), $[\alpha]_D^{25}$ +102.8° (pyridine) gave a positive coloration in the Mg–HCl test. The ultraviolet (UV) spectrum showed maxima at 240 sh, 252, 268, 290 sh, and 344 nm, and the infrared (IR) spectrum exhibited absorption bands due to hydroxyls (3400 $cm^{-1}$), an α,β-unsaturated ketone (1653, 1624 $cm^{-1}$) and aromatic rings (870, 845, 806, 759, 687 $cm^{-1}$). Compound **2** was suggested to be a flavone *C*-glycoside from the characteristic color reaction and spectral properties, and it was not hydrolyzed in 2 N HCl. The bathochromic shifts of the UV bands of **2** with sodium acetate ($\lambda_{II}$ = 7 nm) and aluminum chloride ($\lambda_I$ = 33 nm) suggested the presence of free 5- and 7-dihydroxyls,[10] respectively. The proton nuclear magnetic resonance ($^1$H-NMR) spectrum of **2** in dimethyl sulfoxide

TABLE I. $^1$H-NMR Spectral Data[a]

| | **1** | **2** | **2a** | **2b**[b] |
|---|---|---|---|---|
| Aglycone moieties | | | | |
| H-3 | 6.82 (s) | 6.80 (s) | 6.81 (s) | 6.55 (s) |
| H-8 | 6.56 (s) | 6.56 (s) | 7.16 (s) | 7.26 (s) |
| H-2′ | 6.93 (d, $J$=8.9 Hz) | 7.45 (d, $J$=2.2 Hz) | 7.56 (d, $J$=2.2 Hz) | 7.56 (d, $J$=2.2 Hz) |
| H-3′ | 7.94 (d, $J$=8.9 Hz) | | | |
| H-5′ | 7.94 (d, $J$=8.9 Hz) | 7.10 (d, $J$=8.8 Hz) | 7.13 (d, $J$=8.8 Hz) | 7.07 (d, $J$=8.8 Hz) |
| H-6′ | 6.93 (d, $J$=8.9 Hz) | 7.57 (dd, $J$=8.8, 2.2 Hz) | 7.68 (dd, $J$=8.8, 2.2 Hz) | 7.73 (dd, $J$=8.8, 2.2 Hz) |
| OH | 13.50 (s) | 13.47 (s) | | |
| OMe | | 3.87 (s) | 3.79 (s) | 3.92 (s) |
| | | | 3.86 (s) | |
| | | | 3.90 (s) | |
| | | | 3.93 (s) | |
| OAc | | | | 2.36 (s) |
| | | | | 2.43 (s) |
| | | | | 2.51 (s) |
| Sugar moieties | | | | |
| H-1″ | 5.01 (dd, $J$=11.7, 3.2 Hz) | 5.00 (dd, $J$=11.7, 3.2 Hz) | 4.88 (dd, $J$=11.8, 2.2 Hz) | 4.82 (d, $J$=12.0 Hz) |
| H-2″$_{ax}$ | 2.05 (q, $J$=11.7 Hz) | 2.06 (q, $J$=11.7 Hz) | 2.58 (q, $J$=11.8 Hz) | 1.98 (q, $J$=12.0 Hz) |
| H-2″$_{eq}$ | 1.60 (ddd, $J$=11.9, 5.2, 3.2 Hz) | 1.61 (ddd, $J$=11.9, 5.2, 3.2 Hz) | 1.37 (ddd, $J$=11.8, 5.1, 2.2 Hz) | 1.70 (br d, $J$=12.0 Hz) |
| H-3″ | 3.77 (ddd, $J$=12.7, 5.2, 2.4 Hz) | 3.71 (ddd, $J$=12.7, 5.2, 2.4 Hz) | 3.64 (ddd, $J$=12.7, 5.1, 2.4 Hz) | 5.09 (ddd, $J$=12.6, 5.5, 2.8 Hz) |
| H-4″ | 3.46 (d, $J$=2.4 Hz) | 3.47 (d, $J$=2.4 Hz) | 3.83 (d, $J$=2.4 Hz) | 5.23 (br d, $J$=3.1 Hz) |
| H-5″ | 3.65 (q, $J$=6.4 Hz) | 3.66 (q, $J$=6.4 Hz) | 3.51 (q, $J$=6.3 Hz) | 3.79 (q, $J$=6.6 Hz) |
| H-6″ | 1.18 (d, $J$=6.4 Hz) | 1.19 (d, $J$=6.4 Hz) | 1.15 (d, $J$=6.3 Hz) | 1.19 (d, $J$=6.6 Hz) |
| | | | | 2.00 (s) |
| | | | | 2.21 (s) |

*a*) Measured in DMSO-$d_6$ at 400 MHz, with TMS as an internal standard. The following abbreviations are used: s, singlet; d, doublet; q, quartet; br, broad. *b*) In $CDCl_3$ solution.

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(DMSO)-$d_6$ showed an AMX system due to a 3′,4′-disubstitution, and two singlets due to one proton each at $\delta$ 6.56 and $\delta$ 6.80 attributed respectively to H-8 and H-3,[11] and a sugar portion ($\delta$ 1.19—5.00) (Table I). Consequently, **2** is considered to be a 5,7-dihydroxy-6-*C*-glycosylflavone derivative. Two singlets at $\delta$ 3.87 (3H) and $\delta$ 13.47 (1H) are assigned to an aromatic methoxy group in the B-ring and a chelated hydroxyl at C-5, respectively. In the carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectrum of **2** in DMSO-$d_6$, the chemical shifts of carbon signals in the B-ring agreed with those of diosmetin (3′,5,7-trihydroxy-4′-methoxyflavone)[12]; a methine signal was seen at $\delta$ 94.6 and five quaternary carbons at $\delta$ 157.4, 110.0, 163.7, 156.1, and 103.4 were assigned to C-5, C-6, C-7, C-8a, and C-4a by comparison with those of diosmetin, respectively. The aromatic methine signal ($\delta$ 94.6) or ring A is compatible with that of C-8 ($\delta$ 94.0). The remaining carbon signal at $\delta$ 110.0 in ring A was assigned to C-6 which has undergone a downfield shift of 10.1 ppm owing to *C*-glycosylation.[12] The assignment of the sugar linkage at C-6 was supported by the circular dichroism (CD) spectrum, which showed a positive Cotton effect at 266 nm ($\Delta_\varepsilon$ +4.9, MeOH) for **2**, because a positive Cotton effect at 250—275 nm for *C*-glycosylflavones and acetyl derivatives is indicative of 6-*C*-$\beta$-glycosylflavones[13] (Fig. 1). Tlhe presence of three phenolic hydroxyls in **2** was confirmed by methylation with diazomethane to afford the trimethyl ether (**2a**). These results suggest that **2** is diosmetin 6-*C*-glycoside. The sugar carbon signals of **2** were observed in the region of $\delta$ 17.4—74.4, and the distortionless enhancement by polarization transfer (DEPT) spectra indicated the presence of dideoxyhexose with one methyl, one methylene, and four methine carbons. In the $^1$H–$^1$H shift correlation (COSY) spectrum (Fig. 2), a double doublet ($J$ = 11.7, 3.2 Hz) due to H-1″ (anomeric proton) at $\delta$ 5.00 was coupled to two nonequivalent geminal protons at $\delta$ 2.06 (q, $J$ = 11.7 Hz) and $\delta$ 1.61 (ddd, $J$ = 11.9, 5.2, 3.2 Hz), assigned respectively to H-2″$_{ax}$ and H-2″$_{eq}$. The anomeric proton was established as axial on the basis of the coupling constant ($J$ = 11.7 Hz) between the anomeric proton (H-1″) and the adjacent H-2″$_{ax}$. The observation of cross peaks between the H-2″$_{ax}$, H-2″$_{eq}$ and a resonance at $\delta$ 3.71 (ddd, $J$ = 12.7, 5.2, 2.4 Hz), between resonances at $\delta$ 3.71 and $\delta$ 3.47 (d, $J$ = 2.4 Hz), between resonances at $\delta$ 3.47 and $\delta$ 3.66 (q, $J$ = 6.4 Hz) and between resonances at $\delta$ 3.66 and $\delta$ 1.18 (d, $J$ = 6.4 Hz) permitted the assignments of H-3″, H-4″, H-5″, and 6″-Me, respectively.

The presence of dideoxyhexose was also supported by the fact that the acetylation of **2** gave a pentaacetate (**2b**) having two aliphatic acetyls ($\delta$ 2.00, 2.21) and three phenolic acetyls ($\delta$ 2.36, 2.43, 2.51). A spin-decoupling experiment with **2b** showed that irradiation of the quartet at $\delta$ 3.79 (5″-H), a double double doublet at $\delta$ 5.09 (3″-H), and a broad

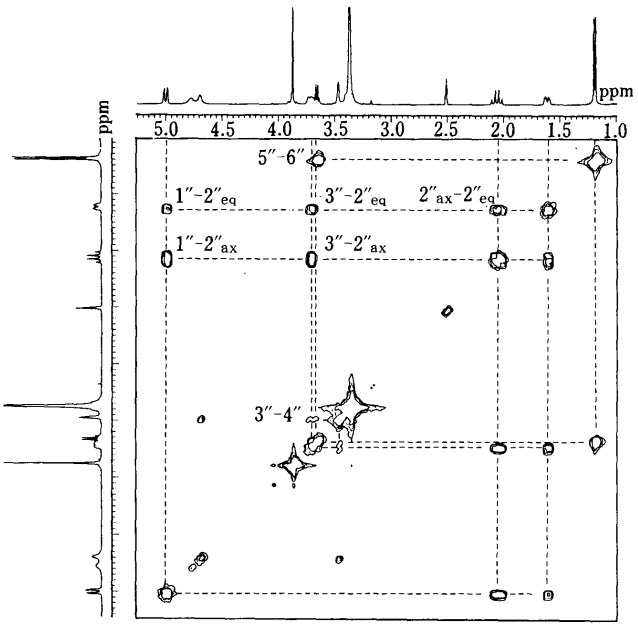


Fig. 2. Contour Map of $^1$H–$^1$H COSY Spectrum for Compound **2**

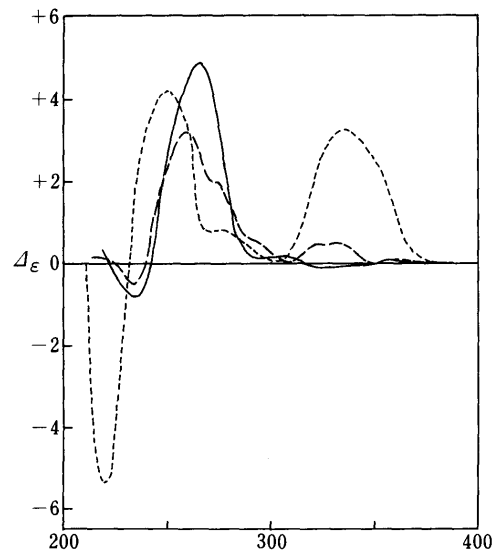


Fig. 1. CD Spectra of Compounds **1** (——), **2** (– – – –), and **2b** (------)

TABLE II. $^{13}$C-NMR Spectral Data for Torosaflavone A (**1**) and Torosaflavone B (**2**)

| | **1**[a] | **2**[b] |
|---|---|---|
| C-2 | 163.8 | 162.30 |
| C-3 | 102.6 | 103.38 |
| C-4 | 181.8 | 181.91 |
| C-4a | 103.4 | 103.42 |
| C-5 | 157.2 (−3.9)[c] | 157.37 (−3.3) |
| C-6 | 109.9 (+11.1) | 110.02 (+11.0) |
| C-7 | 162.1 (−2.0) | 163.67 (−0.7) |
| C-8 | 94.6 | 94.59 |
| C-8a | 156.0 (−1.3) | 156.11 (−1.8) |
| C-1′ | 121.0 | 122.80 |
| C-2′ | 128.4 | 112.89 |
| C-3′ | 115.9 | 146.73 |
| C-4′ | 161.1 | 151.19 |
| C-5′ | 115.9 | 112.06 |
| C-6′ | 128.4 | 118.75 |
| OMe | | 55.71 |
| Sugar moieties | | |
| C-1″ | 70.2 | 70.09 |
| C-2″ | 32.4 | 32.28 |
| C-3″ | 68.4 | 68.42 |
| C-4″ | 69.5 | 69.53 |
| C-5″ | 74.4 | 74.40 |
| C-6″ | 17.4 | 17.37 |

Measured in DMSO-$d_6$ at *a*) 25 MHz and *b*) 100 MHz, with TMS as the internal standard. *c*) Values in parentheses indicate glycosylation shifts.

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TABLE III. Positional and Thermal Parameters for the Nonhydrogen Atoms of Torosaflavone B (**2**)

| Atom | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| C(2) | 0.9566 (3) | 0.7637 (3) | 0.7259 (5) | 2.6 |
| C(3) | 0.9039 (3) | 0.7049 (3) | 0.7981 (6) | 2.7 |
| C(4) | 0.8094 (3) | 0.7196 (2) | 0.8279 (5) | 2.4 |
| C(4a) | 0.7740 (2) | 0.7981 (3) | 0.7661 (5) | 2.3 |
| C(5) | 0.6803 (3) | 0.8188 (2) | 0.7686 (5) | 2.4 |
| C(6) | 0.6467 (3) | 0.8911 (2) | 0.6957 (5) | 2.3 |
| C(7) | 0.7097 (3) | 0.9476 (2) | 0.6289 (6) | 2.6 |
| C(8) | 0.8026 (3) | 0.9308 (3) | 0.6269 (6) | 2.8 |
| C(8a) | 0.8319 (2) | 0.8561 (2) | 0.6911 (5) | 2.4 |
| C(1′) | 1.0548 (3) | 0.7559 (3) | 0.6922 (5) | 2.4 |
| C(2′) | 1.0995 (3) | 0.8187 (3) | 0.6038 (5) | 2.4 |
| C(3′) | 1.1924 (3) | 0.8165 (2) | 0.5831 (5) | 2.4 |
| C(4′) | 1.2430 (3) | 0.7496 (3) | 0.6496 (5) | 2.6 |
| C(5′) | 1.1984 (3) | 0.6854 (3) | 0.7323 (6) | 2.9 |
| C(6′) | 1.1043 (3) | 0.6891 (3) | 0.7529 (6) | 3.2 |
| C(1″) | 0.5437 (3) | 0.9027 (2) | 0.6889 (5) | 2.4 |
| C(2″) | 0.5022 (3) | 0.9312 (3) | 0.8496 (5) | 2.6 |
| C(3″) | 0.3989 (3) | 0.9410 (2) | 0.8256 (5) | 2.4 |
| C(4″) | 0.3819 (3) | 1.0025 (3) | 0.6880 (6) | 2.8 |
| C(5″) | 0.4273 (3) | 0.9701 (3) | 0.5326 (5) | 2.8 |
| C(6″) | 0.4182 (3) | 1.0302 (4) | 0.3912 (6) | 4.6 |
| C(9′) | 1.3890 (3) | 0.6947 (3) | 0.7191 (7) | 3.6 |
| O(1) | 0.9232 (2) | 0.8391 (2) | 0.6761 (4) | 2.7 |
| O(9) | 0.7600 (2) | 0.6669 (2) | 0.9036 (4) | 3.1 |
| O(10) | 0.6207 (2) | 0.7652 (2) | 0.8411 (4) | 3.2 |
| O(11) | 0.6844 (2) | 1.0222 (2) | 0.5607 (5) | 3.6 |
| O(7′) | 1.2380 (2) | 0.8772 (2) | 0.5000 (4) | 3.3 |
| O(8′) | 1.3344 (2) | 0.7542 (2) | 0.6294 (4) | 3.0 |
| O(7″) | 0.5244 (2) | 0.9614 (2) | 0.5609 (4) | 2.8 |
| O(8″) | 0.3567 (2) | 0.9714 (2) | 0.9726 (4) | 3.0 |
| O(9″) | 0.4167 (2) | 1.0828 (2) | 0.7325 (5) | 4.4 |

doublet at $\delta$ 5.23 (4″-H) changed a singlet at $\delta$ 1.19 (5″-Me) and a sharp doublet at $\delta$ 5.23 (4″-H), a sharp doublet at $\delta$ 1.70 ($2''_{eq}$-H) and a singlet at $\delta$ 5.23 (4″-H), and a double doublet at $\delta$ 5.09 ($J$=12.6, 5.5 Hz, 3″-H), respectively. Thus, the configurations of H-3″ and H-4″ were indicated to be axial and equatorial, respectively. However, the stereochemistry of C-5″ was not defined by the absence of coupling between H-4″ and H-5″. The stereochemistry at C-5″ was confirmed by nuclear Overhauser effect (NOE) difference measurement. The H-5″ and H-1″ (anomeric proton) are located at a 1,3-diaxial position in the pyranose ring because NOE was observed at $\delta$ 4.82 (H-1″) (11%) on irradiation at $\delta$ 3.79 (H-5″) in **2b**. According to the above data the structure of the sugar portion is 2,6-dideoxylyxo-hexose (oliose).[14] The assignments of $^{13}$C-NMR signals of **2** were achieved by $^{1}$H–$^{13}$C COSY, as shown in Table II.

X-ray crystallographic structure determination was carried out and the ORTEP drawing is shown in Fig. 3. The final atomic parameters are listed in Table III. Consequently, the absolute configuration of the sugar unit is either $\beta$-D or $\alpha$-L form.

In order to determine the absolute configuration of the sugar in **2**, the dibenzoate (**2c**) was prepared from **2a**. The CD spectrum of **2c** showed a positive chirality of the 3″,4″-dibenzoate groups[15] based on the Newman's projection at C-3″ and C-4″ (Figs. 4 and 5). So, the absolute configuration of oliose in **2** was decided as D form from the Cotton effect of the dibenzoate (**2c**) and as $\beta$-configuration by the conformational analysis of the anomeric proton (H-1″) based on with the $^{1}$H-NMR spectrum.

Therefore, the structure of torosaflavone B (**2**) was

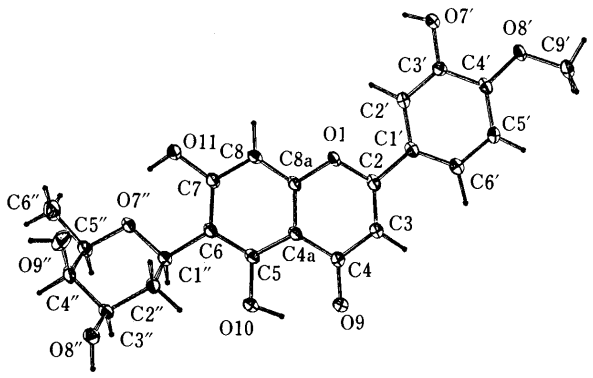


Fig. 3. ORTEP Drawing of Torosaflavone B (**2**)

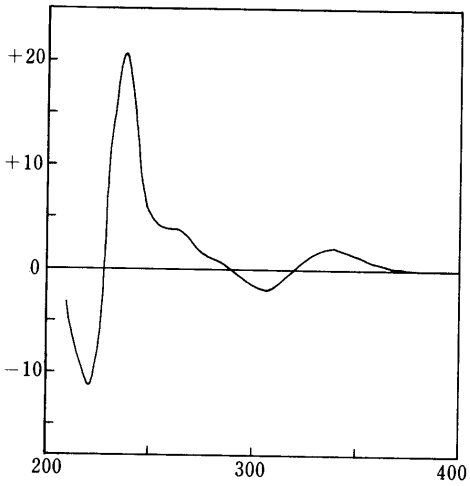


Fig. 4. CD Spectrum of Torosaflavone Trimethyl Ether Dibenzoate (**2c**)

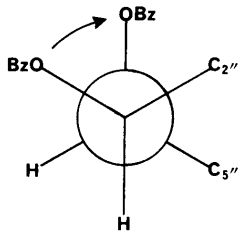


Fig. 5. Newman's Projection

determined to be diosmetin 6-*C*-$\beta$-D-olioside (diosmetin 6-*C*-2,6-dideoxy-$\beta$-D-lyxo-hexoside).

Compound **1** was obtained as yellow needles, mp 170 °C, $C_{21}H_{20}O_8$ ($M^+$ 400.1134), $[\alpha]_D^{25}$ +107.1° (pyridine). The UV spectrum of **1**, with maxima at 272 and 333 nm, was similar to that reported for apigenin. The bathochromic shifts of the UV bands of **1** with sodium acetate ($\lambda_{II}$=7 nm) and aluminum chloride ($\lambda_{I}$=20 nm) showed the presence of 7- and 5-hydroxyls in a flavone skeleton, respectively. The $^{1}$H-NMR spectrum of **1** showed an $A_2B_2$ system due to 4′-substitution in the B-ring, two singlets of one proton each at $\delta$ 6.56 and $\delta$ 6.82 attributed H-8 and H-3, respectively, and sugar signals which agreed very well with those of **2**. Thus, **1** was considered to be the 6-*C*-olioside of apigenin. The absolute configuration of the sugar in **1** was decided as $\beta$-D by comparing its NMR, CD spectra and specific rotation with those of **2**. Based on these findings, the structure of **1** was established as apigenin 6-*C*-$\beta$-D-olioside.

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Recently, a *C*-glycosylflavone having a dideoxy sugar (boivinose) was reported from *Alternanthera philoxeroides* (Amaranthaceae).[16]

## Experimental

All the melting points were taken on a Yanagimoto micro-melting-point apparatus and are uncorrected. The UV and CD spectra were obtained in MeOH with Hitachi 200-10 and JASCO J-600 spectrophotometers, respectively, and the IR spectra were recorded on a JASCO IR A-2 spectrophotometer. The $^1$H- and $^{13}$C-NMR spectra were taken on JEOL GX-400 and JEOL FX-100 spectrometers, respectively, using tetramethylsilane (TMS) as an internal standard. The mass spectra (MS) were obtained on a Hitachi M-80B spectrometer. Column chromatography was carried out with silica gel (Wako gel C-200, Wako Pure Chemical Industry Ltd.) or Sephadex LH-20 (25—100 $\mu$m, Pharmacia Fine Chemical Co., Ltd.). Preparative thin layer chromatography (TLC) was carried out with pre-coated Silica gel 60 (2 mm, Merk).

**Extraction and Isolation** The leaves of *Cassia torosa* CAV. were collected at the Drug Plant Garden, College of Science and Technology, Nihon University, during July to August 1987. The dried leaves (5.5 kg) were extracted with MeOH (77 l × 3) under reflex. The MeOH extract was concentrated *in vacuo* to give a dark green mass, which was then dissolved in $H_2O$. This solution was extracted with $Et_2O$, AcOEt, and 1-BuOH, successively. The $Et_2O$ solution was concentrated to give a dark mass (11.5 g), which was then chromatographed on $SiO_2$ with $CHCl_3$ to give fractions 1—3 and with $CHCl_3$–MeOH mixture to give fractions 4—12, respectively. Fraction 5 (3% MeOH–$CHCl_3$) (1.6 g) and fraction 6 (1.5 g) were each chromatographed on Sephadex LH-20 and eluted with MeOH to give **2** (67 mg) and **1** (66 mg), respectively.

**Torosaflavone A (1)** Recrystallization (MeOH) gave pale yellow needles, mp 171—172 °C, $[\alpha]_D^{25}$ +107.1° ($c$=0.93, pyridine). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 215 (4.25), 272 (4.20), 333 (4.09); $\lambda_{max}^{MeOH+AcONa}$ nm: 221, 279, 313, 331, 396; $\lambda_{max}^{MeOH+AcONa+H_3BO_3}$ nm: 221, 271, 338; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 221, 280, 353, 383 sh; $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 221, 280, 303, 349, 388 sh. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1654, 1626, 1573, 1508, 1490, 1444, 862, 834. CD ($c=4.25\times10^{-5}$; MeOH) $\Delta\varepsilon^{24}$: 351 (+0.2), 335 (0), 321 (−0.4), 307 (0), 293 (+0.7), 268 (+4.6), 239 (0), 234 (−0.5), 221 (0). EI-MS (in beam) $m/z$: 400 ($M^+$, 7.5%), 382 ($M^+-H_2O$, 13.7), 364 ($M^+-2H_2O$, 3.4), 338 ($M^+-H_2O-C_2H_5O$, 11.6), 307 ($M^+-H_2O-C_3H_7O_2$, 100), 295 ($M^+-C_4H_9O_3$, 57.5), 283 ($M^+-C_5H_9O_3$, 57.5), 283 ($M^+-C_5H_9O_3$, 8.9), 270 ($M^+-C_6H_{10}O_3$, 16.4). High-resolution MS $m/z$: Calcd for $C_{21}H_{20}O_8$: 400.1156. Found: 400.1134. The $^1$H- and $^{13}$C-NMR data are shown in Table I and II, respectively.

**Torosaflavone B (2)** Recrystallization (MeOH) gave yellow prisms, mp 240—241.5 °C, $[\alpha]_D^{25}$ +102.8° ($c$=1.02, pyridine). UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 240 sh (4.24), 252 (4.26), 268 (4.27), 290 sh (4.06), 344 (4.32); $\lambda_{max}^{MeOH+AcONa}$ nm: 275, 315, 375; $\lambda_{max}^{MeOH+AcONa+H_3BO_3}$ nm: 253 sh, 268, 347; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 218, 277, 350, 380 sh; $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 240 sh, 258 sh, 278, 293, 356, 380. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1653, 1624, 1577, 1519, 1496, 1478, 1444, 870, 845, 806, 759, 709, 687. CD ($c=7.18\times10^{-5}$: MeOH) $\Delta\varepsilon^{24}$: 356 (+0.1), 347 (0), 327 (−0.1), 317 (0), 307 (+0.2), 266 (+4.9), 242 (0), 233 (−0.8), 221 (0). EI-MS (in beam) $m/z$: 430 ($M^+$, 31.4%), 412 ($M^+-H_2O$, 7.2), 394 ($M^+-2H_2O$, 7), 367 ($M^+-H_2O-C_2H_5O$, 5.1), 342 ($M^+-C_4H_8O_2$, 5.1), 342 ($M^+-C_4H_8O_2$, 40.9), 337 ($M^+-H_2O$, 5.1), 342 ($M^+-H_2O-C_3H_7O_2$, 100), 325 ($M^+-C_4H_9O_3$, 44.8), 313 ($M^+-C_5H_9O_3$, 16.7), 300 ($M^+-C_6H_{10}O_3$, 28.3). High-resolution MS (in beam) $M/z$: Calcd for $C_{22}H_{22}O_9$: 430.1261. Found: 430.1236. The $^1$H- and $^{13}$C-NMR data are shown in Tables I and II, respectively.

**Methylation of 2** A solution of **2** (25 mg) in MeOH (4 ml) was methylated with $CH_2N_2$ in $Et_2O$ at 4 °C for 18 h, then the solution was evaporated to give a colorless residue, which was purified by preparative TLC ($CHCl_3$–MeOH, 9:1), to afford trimethyl ether (**2a**) (16 mg) as an amorphous powder. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 215 (4.55), 242 (4.40), 261 sh (4.32), 332 (4.39). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3400, 1632, 1599, 1513, 842, 861, 842, 820, 792, 768. CD ($c=3.58\times10^{-5}$: MeOH) $\Delta\varepsilon^{24}$: 337 (+1.0), 318 (0), 307 (−1.0), 290 (0), 283 (+1.1), 262 (+3.0), 227 (0). High-resolution MS (in beam) $m/z$: Calcd for $C_{25}H_{28}O_9$: 472.1731. Found 472.1704. $^1$H-NMR data are shown in Table I.

**Acetylation of 2** A solution of **2** (5 mg) in a mixture of $Ac_2O$ (1 ml) and pyridine (1 ml) was allowed to stand at 90 °C for 2 h and evaporated to dryness *in vacuo*. The residue was purified by preparative TLC (*n*-hexane–AcOEt, 2:3) and recrystallized from *n*-hexane–AcOEt to give colorless needles, mp 140—142 °C. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 222 (4.53), 255 (4.28), 317 (4.51). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1772, 1749, 1634, 1580, 1512. CD ($c=3.59\times10^{-4}$, MeOH) $\Delta\varepsilon^{22}$: 335 (+3.3), 302 (0), 277 (+0.8), 250 (+4.2), 232 (0), 220 (−5.3). High-resolution MS (in beam) $m/z$: Calcd for $C_{32}H_{32}O_{14}$: 640.1789. Found 640.1829. $^1$H-NMR data are shown in Table I.

**Benzoate (2c) from 2a** Benzoyl chloride (35 mg) was added to a pyridine solution (1 ml) of **2a** (10 mg), and the mixture was allowed to stand for 18 h at room temperature then evaporated *in vacuo*. The residue was purified by preparative TLC ($C_6H_6$–AcOEt, 3:2) and recrystallized from MeOH–$H_2O$ to give a colorless powder, mp 134—136 °C. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 231 (4.61), 263 sh (4.19), 282 (3.95), 332 (4.36). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 1723, 1643, 1601, 1515, 1452, 1422. CD ($c=2.09\times10^{-5}$: MeOH) $\Delta\varepsilon^{23}$: 338 (+2.2), 319 (0), 306 (−2.1), 290 (0), 264 (+3.9), 238 (+20.5), 228 (0), 222 (−11.6). $^1$H-NMR ($CDCl_3$) $\delta$: 1.33 (3H, d, $J$=6.7 Hz, 5″-Me), 1.94 (1H, ddd, $J$=12.2, 5.1, 2.2 Hz), 3.28 (1H, q, $J$=12.2 Hz, H-2″$_{ax}$), 4.17 (1H, q, $J$=6.7 Hz, H-5″), 3.97, 4.00, 4.01, 4.07 (each 3H, s, OMe × 4), 5.32 (1H, dd, $J$=11.7, 2.2 Hz, H-1″), 5.48 (1H, ddd, $J$=12.2, 5.1, 2.9 Hz, H-3″), 5.61 (1H, d, $J$=2.9 Hz, H-4″), 6.69 (1H, s, H-8), 6.81 (1H, s, H-3), 6.98 (1H, d, $J$=8.8 Hz, H-5′), 7.35 (1H, d, $J$=2.0 Hz), 7.56 (1H, dd, $J$=ε 3, 2.0 Hz, H-6′), 7.30, 7.56 (each 2H, t, $J$=8.3 Hz, Bz-3, 5), 7.45, 7.65 (each 1H, tt, $J$=8.3, 1.5 Hz, Bz-4), 7.83, 8.28 (each 2H, dd, $J$=8.3, 1.5 Hz, H-2, 6). High-resolution MS (in beam) $m/z$: Calcd for $C_{39}H_{36}O_{11}$: 680.2254. Found 680.2221.

**Crystal Data of 2** $C_{22}H_{22}O_9$, $M_r$=430.1, orthorhombic, space group $P2_12_12_1$, $a$=14.720 (6), $b$=15.857 (6), $c$=8.189 (1) Å; $V$=1911 Å$^3$, $Z$=4, $D_c$=1.496 g·cm$^{-3}$, (Cu$K_\alpha$)=15405 Å. A total of 2155 unique independent intensities were measured within the range $3°<2\theta<150°$ on a four-circle diffractometer (Rigaku AFC-5). The structure was solved by the direct method using MULTAN 80 (UNICS III system) and refined by the least-squares method, using the 1657 reflections for which $|F_o|>3\sigma/F_o|$. The final $R$ value was 3.73%.

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