Phytochemistry, Vol. 27, No. 1, pp. 259–266, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00

SEVEN PRENYLATED FLAVONOL GLYCOSIDES FROM TWO *EPIMEDIUM* SPECIES

TOSHIO FUKAI and TARO NOMURA

Faculty of Pharmaceutical Sciences, Toho University, Funabashi, Chiba 274, Japan

(*Received* 15 *April* 1987)

Key Word Index—*Epimedium grandiflorum; E. sempervirens*; Berberidaceae; ikarisosides A, B, C, D, E and F; icarisid II; prenylated flavonol glycosides; FABMS; ^{13}C NMR; ^{1}H NMR.

Abstract—Five new flavonol glycosides, ikarisosides B, C, D, E and F were isolated from the roots of *Epimedium grandiflorum* and their structures elucidated as 8-prenylkaempferol-3-*O*-β-glucosyl (1 → 2)-α-rhamnoside, 8-prenylkaempferol 3-*O*-β-glucosyl(1 → 2)-α-rhamnoside]-7-*O*-β-glucoside, 8-prenylkaempferol 3-*O*-α-(4″ acetyl) rhamnoside, 6″,6″-dimethylpyrano(2″,3″: 7,8) kaempferol 3-*O*-α-rhamnoside and 8-prenylkaempferol 3-*O*-β-xylosyl(1 → 2)-α-rhamnoside, respectively. Ikarisoside A was also isolated from the same material and confirmed as the hydrolysis product of epimedoside A. From the root *E. sempervirens*, ikarisosides A, C and E, as well as icarisid II, were isolated. Ikarisoside A and icarisid II were isolated for the first time as natural products.

INTRODUCTION

Several *Epimedium* species have been used as tonics in Chinese herbal medicine. The constituents of these plants have been studied by many investigators and a series of prenylated flavonol glycosides have been isolated [1–9]. We have already reported a series of isoprene-substituted flavonoids from species of the Moraceae [10]. In continuation of these studies we report here the isolation and characterization of an additional seven prenylated flavonol glycosides from the roots of *Epimedium grandiflorum* Morren and *E. sempervirens* Nakai.

RESULTS AND DISCUSSION

From an ethanol extract of the root of *E. grandifolrum* Morren, ikarisoside A (**1**) was isolated as well as five new compounds, ikarisosides B (**2**), C (**3**), D (**4**), E (**5**) and F (**6**).

Ikarisoside A (**1**). The EIMS of **1** showed the molecular ion peak at *m/z* 500, and the ^{13}C NMR spectrum indicated the presence of 26 carbons (Table 1). The compound was also negative to the zirconium oxychloride–citric acid test, while positive to the zirconium oxychloride–citric acid–hydrogen chloride test [11, 12]. The ^{13}C NMR spectrum of **1** was analysed by the off-resonance decoupling technique as well as by comparing it with the ^{13}C NMR spectra of model compounds, such as kaempferol (**7**), epimedoside A (**8**) [6] and other flavonol glycosides [13]. In these spectra, the signal for the C-2 of **1** appeared to be a more downfield shift than that for the C-2 of **7**, whereas the C-3 of **1** appeared to be an upfield shift (Table 1). These results suggest that the **1** is a flavonol 3-glycoside.

The EIMS of **1** showed a characteristic ion peak at *m/z* 354 which could be attributed to a prenylkaempferol ion. The location of the prenyl group at the C-8 position was supported by the negative Gibbs test and the chemical shift value of the carbon atom at the C-6 position (δ97.9) [13]. The 8-prenylated structure for **1** was confirmed by the derivation of ikarisoside E (**5**) from **1** as described in the case of **5**. The sugar moiety of **1** was identified as rhamnose by comparative examination of the ^{13}C NMR spectra of **1** and model compounds, such as quercetin 3-*O*-rhamnoside [13] (Table 1). The α-anomeric centre is evident from the ^{13}C-H coupling constant at the C-1″ position of **1** ($J_{^{13}C1''-H1''}$ = 173 Hz) [14–16]. From the above results and consideration of the ^{1}H NMR spectrum of **1**, ikarisoside A may be characterized as 8-prenylkaempferol 3-*O*-α-rhamnopyranoside. While **1** has been recorded as a hydrolysis product of epimedoside A (**8**) [6], this is its first report as a natural product.

Ikarisoside B (**2**). The FABMS of **2** showed peaks at *m/z* 685 $[M + Na]^+$, 663 $(M + H]^+$, and the ^{13}C NMR spectrum indicated the presence of 32 carbons (Table 1). These results revealed the molecular formula of **2** to be $C_{32}H_{38}O_{15}$. The ^{13}C NMR spectrum of **2** was analysed and compared with that of epimedoside A (**8**). The chemical shift values of the carbon atoms of **2** were similar to those of the relevant carbon atoms of **8** except for the signals of the carbon atoms of the sugar moieties. The sugar moieties were identified as rhamnose and glucose by comparative examination of the ^{13}C NMR spectra of **2** and model compounds [13] (Table 1). In the ^{1}H NMR spectrum of **2**, the signal for the proton at C-6 was observed at δ6.33, while that of the relevant proton of **8** was at δ6.63. From this result, there is no sugar moiety at the C-7 position [17]. In the ^{13}C NMR spectrum of **2**, one of the sugar carbon signals was observed at δ80.8, suggesting that the sugar moiety is a disaccharide. To elucidate the sugar sequence, comparison of the FABMS of **2** and **8** was carried out. The FABMS of **2** showed the fragment ions at *m/z* 501 $[M + H\text{-glucosyl} + H]^+$ and 355 $[M + H\text{-glucosyl} + H\text{-rhamnosyl} + H]^+$, while that of **8** showed the ions at *m/z* 517 $[M + H\text{-rhamnosyl} + H]^+$, 501 $[M + H\text{-glucosyl} + H]^+$ and 355 $[M + H - \text{glucosyl} + H - \text{rhamnosyl} + H]^+$, indicating the sequential loss of glucosyl and then rhamnosyl moieties together with the absence of an initial loss of a rhamnosyl moiety, and hence

Table 1. ^{13}C NMR data in DMSO-d_6 at 50° for 1–9

C	7*	1	2	3	4	6	8	9	C	5
2	146.6	156.3	156.1	156.7	156.3	156.2	156.9	156.2	2	156.5[b]
3	135.5	133.6	133.7	134.0	133.2	133.6	133.7	133.8	3	133.8
4	175.7	177.2	177.0	177.3	176.8	177.2	177.4	177.1	4	177.1
4a	102.8	103.7	103.5	103.8	103.3	103.6	103.4	103.6	4a	100.3
5	160.5	158.2	158.0	158.3	158.1	158.1	158.3	158.1	5	159.9
6	98.0	97.9	97.8	97.8	98.2	97.9	97.7	97.8	6	98.6
($J_{^{13}C6\text{-}OH5}$)	(>4 Hz)†		(5.5 Hz)			(6.6 Hz)				
7	163.8	160.8	160.9	159.7	161.9	160.8	159.7	160.9[b]	7	157.9[b]
8	93.3	105.5	105.4	105.2	105.5	105.8	105.1	105.4	8	104.6
8a	156.0	153.1	153.0	152.3	153.1	153.0	152.3	153.8	8a	149.8
9		21.7	21.0	21.3	21.1	21.1	21.3	21.0	4′	113.3
10		121.8	121.7	121.7	122.0	121.8	121.6	121.7	5′	127.3
11		130.3	130.2	130.3	130.1	130.2	129.9	130.3	6′	77.8
12		17.6	17.6	17.7	17.6	17.6	17.7	17.6	7′,8′	27.6
13		25.2	25.2	25.2	25.2	25.2	25.2	25.2		
1′	121.5	120.3	120.0	119.7	120.1	120.1	120.1	121.8	1′	119.5
2′,6′	129.3	129.8	129.8	129.8	129.7	129.7	129.9	129.7	2,6′	129.9
3′,5′	115.2	114.9	114.8	115.0	114.9	114.9	114.9	115.5	3′,5′	114.7
4′	159.0	159.2	159.2	159.7	159.5	159.3	159.3	160.5[b]	4′	159.9
OMe								55.2		
1″		101.5	100.4	100.3	100.9	100.5	100.2	101.4	1″	101.5
($J_{^{13}C1''\text{-}H1''}$)		(173 Hz)	(176 Hz)	(178 Hz)		(176 Hz)				
2″		69.8[a]	80.8	80.6	69.7	80.1	70.1[a]	69.7[a]	2″	69.7[a]
3″		70.2[a]	69.8[a]	69.6[a]	67.7[a]	69.1[a]	69.5[a]	70.0[a]	3″	70.1[a]
4″		70.3[a]	70.0[a]	70.0[a]	73.0	69.98[a]	70.2[a]	70.2[a]	4″	70.3
5″		71.0[a]	71.3[a]	71.4[a]	67.6[a]	70.00[a]	70.9[a]	70.8[a]	5″	70.9[a]
6″		17.3	17.2	17.2	17.0	17.2	17.3	17.3	6″	17.2
OAc					20.7					
					169.0					
1‴			105.8	105.4		105.5	101.4‡			
($J_{^{13}C1'''\text{-}H1'''}$)			(159 Hz)	(167 Hz)		(155 Hz)				
2‴			73.5	73.6[b]		73.4	73.1			
3‴			76.2	76.3[c]		75.9	76.4			
4‴			69.0	69.2[a]		71.5	69.7[a]			
5‴			75.9	76.0[c]		65.5	76.8			
6‴			60.2	60.4[d]			60.5			
1⁗				100.6‡						
($J_{^{13}C1''''\text{-}H1''''}$)				(162 Hz)						
2⁗				73.1[b]						
3⁗				76.3[c]						
4⁗				69.5[a]						
5⁗				76.8[c]						
6⁗				60.5[d]						

[a–d]Assignments may be interchanged in each column.

*Measured at 23°, reference standard: centre of DMSO-d_6 = δ_C 39.20 ppm.

†Wehrli could not observe this coupling in the case of quercetin (instrument: 20 MHz, digital resolution of 1 Hz) [23], but we observed as broad doublet signals in this case (at 23°, instrument: 100.4 MHz, digital resolution of 0.24 Hz, 60 mg in 0.6 ml of the solvent). The value was obtained by using of long-range selective ^{1}H decoupling (LSPD) [24] with irradiation of the C-8 proton (δ 6.48) [C6 (*br d*, $W_{1/2}$ = *ca* 11 and 12 Hz of the signals → *br d*, $W_{1/2}$ = *ca* 5 and 6 Hz). Coupling constant $J_{^{13}C6,H8}$ = 4.8 Hz was also observed by the method with irradiation of the 5-hydroxy-proton (δ 12.53) [C6 (*br d*, *J* = 157.23 Hz → *dd*, *J* = 4.76 and 162.01 Hz. C4a (*br t*, *J* = 5.13 Hz → *dd*, *J* = 4.53 and 5.74 Hz; $W_{1/2}$ = 1.7 – 2.2 Hz of the signals)].

‡7-*O*-Glucosyl moiety.

the presence of a disaccharide chain attached to the aglycone with glucose as the terminal sugar. The sugar sequence was further supported by the relaxation time (T_1) for the disaccharide moiety (Table 2). The relatively larger values of glucose carbon atoms indicate the glucose unit is terminal [18]. The linkage of the sugar unit was confirmed by consideration of the following acetylation shift values of rhamnosyl moiety. All the proton signals of the rhamnosyl moieties of **1**, **1a**, **2** and **2a** were assigned by decoupling experiments. By comparing the ^{1}H NMR spectrum of **1** with that of **1a**, the acetylation of the C-2″, 3″ and 4″ hydroxyl groups was found to cause downfield

Table 2. Relaxation time measurements for disaccharide moiety of **2** in DMSO-d_6 at 30.3 ± 0.20°*

C	Rhamnose ppm	Rhamnose T_1(sec)	Glucose ppm	Glucose T_1(sec)
1	100.7	0.21	105.8	0.27
2	81.0	0.22	73.6	0.27
3	70.1[a]	0.21	76.1	0.27
4	71.5[a]	0.21	69.1	0.28
5	69.9[a]	0.21	76.4	0.27
6	17.1	0.51	60.3	0.17

[a]assignment may be interchanged.

*Reference standard: centre of DMSO-d_6 = δ_C39.25 ppm from TMS at 100.4 MHz.

Table 3. Acetylation shifts on ^{1}H NMR spectra of rhamnosyl moieties in DMSO-d_6 at 50°* for **1**–**4** and **6**

	1	2	3	4†	6
H-1″	0.10	−0.06	−0.05	0.01	−0.09
H-2″	1.51	0.23	0.22	0.04	0.26
H-3″	1.59	1.51	1.72	0.22	1.53
H-4″	1.61	1.50	1.51	1.53	1.56
H-5″	0.11	−0.16	−0.24	0.14	−0.02
H-6″	−0.04	−0.16	−0.17	−0.11	−0.13

*$\Delta_{\delta\ \text{acetate-flavonol}}$.

†$\Delta_{\delta 4\text{-}1}$.

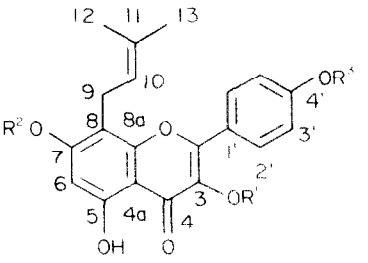
shifts (1.51–1.61 ppm) of the relevant protons. On the other hand, in the case of **2a**, the protons at the C-3″ and 4″ positions showed similar downfield shifts (1.50–1.51 ppm), while the proton at the C-2″ position showed a smaller shift (0.23 ppm) (Table 3). These results demonstrated that the terminal glucose was linked to the rhamnose unit by a (1 → 2) linkage. The ^{1}H NMR spectrum of **2** exhibited a signal at δ4.29 (J = 8 Hz) assignable to an anomeric proton of glucose indicating a β-orientation. The α-anomeric center of the rhamnose moiety was confirmed by the ^{13}C-H coupling constant value ($J_{^{13}C1''\text{-}H1''}$ = 176 Hz) [14–16]. From the above results, ikarisoside B can be characterized as 8-prenylkaempferol 3-*O*-[β-glucopyranosyl(1 → 2)-α-rhamnopyranoside] (**2**).

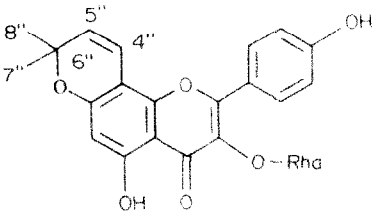
Ikarisoside C (**3**). The FABMS of **3** showed peaks at m/z 847 $[M+Na]^+$, 825 $[M+H]^+$ and the ^{13}C NMR spectrum indicated the presence of 38 carbons (Table 1). These results revealed the molecular formula of **3** to be $C_{38}H_{48}O_{20}$. In the ^{13}C NMR spectrum of **3**, the chemical shift values of the carbon atoms were similar to those of the relevant carbon atoms of **2** except for the signals of carbon atoms in the additional sugar moiety, which was identified as glucose by comparing the spectrum with the spectra of model compounds [13] (Table 1). The FABMS of **3** showed the fragment ions at m/z 663 $[M+H-\text{glucosyl}+H]^+$, 517 $[M+H-\text{glucosyl}+H-\text{rhamnosyl}+H]^+$ and 355 $[M+H-\text{glucosyl}+H-\text{glucosyl}+H-\text{rhamnosyl}+H]^+$. In the ^{1}H NMR spectrum of **3**, signal of the proton at the C-6 position was observed at δ6.62. From the above results, ikarisoside C (**3**) was suggested to be 7-*O*-glucosylikarisoside B. The 7-*O*-glucoside structure was confirmed by consideration of the chemical shift value (δ4.99) of the anomeric proton at the C-1″ ″ position [19]. In the case of the 3-*O*-glucoside, the relevant anomeric proton would have been observed at δ5.7–6.2 [19]. The linkage of the disaccharide moiety was confirmed by consideration of the acetylation shift values of the rhamnose proton (Table 3) and the orientation of the anomeric centres were confirmed by the ^{1}H and ^{13}C NMR spectra as described in the case of **2**. From the above results, ikarisoside C and be characterized as 8-prenylkaempferol 3-*O*-[β-glucopyranosyl (1 → 2)-α-rhamnopyranosidel]-7-*O*-B-glucopyranoside (**3**).

Ikarisoside D (**4**). The EIMS of **4** showed a molecular ion peak at m/z 542, and the ^{13}C NMR spectrum indicated the presence of 28 carbons (Table 1). The molecular formula of **4** seems to be $C_{28}H_{30}O_{11}$. The ^{1}H NMR spectrum indicated the presence of an acetyl moiety. In the ^{13}C NMR spectrum of **4**, the chemical shift values of the carbon atoms were similar to those of the relevant carbon atoms of **1** except for the carbon atom signals of an additional acetyl group and the signals of the rhamnosyl carbons at the C-3″, 4″ and 5″ positions. The proton signals of the rhamnosyl moiety of **4** were assigned by a decoupling experiment. In comparison of the ^{1}H NMR spectrum of **4** with that of **1**, the proton at the C-4″ position of **4** showed a downfield shift (1.53 ppm). These results suggest ikarisoside D to be 4″-acetylikarisoside A. The α-anomeric centre was further supported by comparative examination of the chemical shift values of the rhamnosyl carbon atoms of **4** with those of the calculated chemical shift values of α-(4-acetyl) rhamnosyl and β-(4-acetyl) rhamnosyl moieties [13, 16]. From the above results, ikarisoside D is characterized as 8-prenylkaempferol 3-*O*-α-(4″-acetyl) rhamnopyranoside (**4**).

Ikarisoside E (**5**). The EIMS of **5** showed a molecular ion peak at m/z 498, and the ^{13}C NMR spectrum indicated the presence of 26 carbons (Table 1). The molecular formula of **5** seems to be $C_{26}H_{26}O_{16}$. The ^{1}H NMR spectrum showed the presence of a 2,2-dimethylchromene ring in the structure. From the spectral data, **5** seems to be dehydroikarisoside A. In order to corroborate the structure, the **5** was derived from **1** by treating **1** with palladium chloride in 90% aqueous methanol solution [20]. The angular structure **5** for ikarisoside E (**5**) was supported by the consideration of the acetylation shifts of the chromene olefinic protons in ikarisoside E peracetate (**5a**) (Table 4). These changes are of the same shift and the same order of magnitude as those observed by many investigators for similar compounds [21]. From the above results, ikarisodie E can be characterized as 6″, 6″-dimethylpyrano(2″, 3″:7, 8)-kaempferol 3-*O*-α-rhamnopyranoside (**5**).

Ikarisoside F (**6**). The FABMS of **6** showed characteristic ion peaks at m/z 633 $[M+H]^+$, 501 $[M+H-\text{xylosyl}+H]^+$, 355 $[M+H-\text{xylosyl}+H-\text{rhamnosyl}+H]^+$ and the ^{13}C NMR spectrum indicated the presence of 31 carbons (Table 1). These results revealed the molecular formula of **6** to be $C_{31}H_{36}O_{14}$. The chemical shift values of the carbon atoms of **6** were similar to those of the relevant carbon atoms of **2** except for the signals of the carbon atoms of the terminal sugar moiety. The sugar moieties were identified as rhamnose and xylose by comparative examination of the ^{13}C NMR spectra of **6** and model compounds [13] (Table 1). In the ^{1}H NMR





1 R^1 = Rha, R^2 = R^3 = H

2 R^1 = Rha $\xrightarrow{2}$ Glc, R^2 = R^3 = H

3 R^1 = Rha $\xrightarrow{2}$ Glc, R^2 = Glc, R^3 = H

4 R^1 = Rha (Ac − 4″), R^2 = R^3 = H

5

6 R^1 = Rha $\xrightarrow{2}$ Xyl, R^2 = R^3 = H

8 R^1 = Rha, R^2 = Glc, R^3 = H

9 R^1 = Rha, R^2 = H, R^3 = Me

10 R^1 = Rha, R^2 = Glc, R^3 = Me

Table 4. Chemical shifts (ppm) for H-4″ and H-5″ in 5 and **5a**

Compound	H-4″	H-5″
5	6.73	5.73
5a	6.81	5.92
Δ	−0.08	−0.19

spectrum of **6**, a signal for the proton at the C-6 position was observed at δ6.28. From the above results, **6** is suggested to be 8-prenylkaempferol 3-*O*-xylosyl-rhamnoside. The linkage of the disaccharide moiety was confirmed by consideration of the acetylation shift values of the rhamnose protons (Table 3), and the orientations of the anomeric centres were confirmed by the ^1H and ^{13}C NMR spectra as described in the case of **2**. From the above results, ikarisoside F can be characterized as 8-prenylkaempferol 3-*O*-[β-xylopyranosyl (1 → 2)-α-rhamnopyranoside] (**6**).

In addition to the above compounds, epimedoside A (**8**) [6], icarisid II (**9**) [1, 9] and icariin (**10**) [1, 7, 9] were isolated. **9** was isolated for the first example as a natural product (**9** is also reported from *E. sagittatum* [9] (*Abstract of the papers of the 33rd Annual Meeting of Japanese Society of Pharmacognosy* (1986), Sakato, pp. 25, 84).

EXPERIMENTAL

All mps are uncorr. The ^1H NMR and ^{13}C NMR spectra measured with TMS as int. ref. were run at 400 MHz (digital resolution: 0.18 Hz) and 100.4 MHz (digital resolution: 0.73 Hz), respectively. FABMS were measured on a JEOL JMS-DX 303 mass spectrometer, collision gas Xe (ion gun conditions: 6 KV and 10 mA) and matrix glycerol or thioglycerol. For TLC (silica gel), Wakogel B-5FM (Wako) was used. For prep. TLC (silica gel), A: Wakogel B-5F (Wako), B: Kieselgel 60 PF_{254} gipshaltig (Merk) and C: MN-Kieselgel G UV_{254} (Macherey Nagel), and for CC (silica gel), Wakogel C-200 (Wako).

Plant material. Epimedium grandiflorum Morren was collected in the neighbourhood of Tsukui, Kanagawa prefecture, Japan, in June, 1984. *E. sempervirens* Nakai was collected in the neighbourhood of Sayo, Hyogo prefecture, Japan, in May, 1984. These materials were identified by Dr K. Suzuki, School of Science, Tokyo Metropolitan University and Dr N. Sahashi, Faculty of Pharmaceutical Sciences, Toho University. The samples have been deposited in the herbarium of Toho University.

Isolation of flavonol glycosides from the root of E. grandiflorum. The roots of *E. grandiflorum* (fr. wt 1.9 kg) were exhaustively extracted with EtOH within 10 hr after collection. Evaporation of the soln to dryness yielded 54.4 g of residue. The EtOH extract was chromatographed on deactivated silica gel [22] (370 g) using C_6H_6 (saturated with H_2O)–MeOH (1:0 → 1:1) as an eluent, each fraction (eluted vol. 500 ml) being monitored by TLC. Fraction 35 eluted with C_6H_6(H_2O)–MeOH (9:1) was evap. to give 1.4 g of residue, from the where ikarisoside E (**5**, 26 mg, 1.4×10^{-3}% yield from the material) and ikarisoside D (**4**, 38 mg, 2×10^{-3}%) were obtained using prep. TLC [solvent systems, $CHCl_3$–MeOH (5:1; B), $CHCl_3$–Me_2CO–MeOH (8:1:1; A), C_6H_6–Me_2CO (1:1; A)]. Fractions 37 and 38 eluted with C_6H_6(H_2O)–MeOH (9:1) and fraction 39 with C_6H_6(H_2O)–MeOH (4:1) were evap. to give 5.3 g of residue, which was dissolved in MeOH and allowed to stand at room temp. giving a yellow ppt, which was recryst. from MeOH to give ikarisoside A (**1**, 840 mg, 4.4×10^{-2}%). Fraction 42 eluted with C_6H_6(H_2O)–MeOH (4:1) was evap. to give 3.4 g of residue, which was rechromatographed on a Sephadex LH-20 column

using MeOH–H_2O (4:1) to give ikarisoside F (**6**, 190 mg, 1×10^{-2}%). Fraction 43 eluted with $C_6H_6(H_2O)$–MeOH (4:1) was evapd to give 2.5 g of residue, which was purified by prep. TLC [$CHCl_3$–MeOH (3:1), A: $CHCl_3$–MeOH (4:1), B] to give ikarisoside B (**2**, 520 mg, 2.7×10^{-2}%) and ikarisoside F (**6**, 128 mg, 6.7×10^{-3}%). Fraction 44 eluted with $C_6H_5(H_2O)$–MeOH (1:1) was evapd to give 14 g of residue, and a part of the residue (1.2 g) was purified by prep. TLC [$CHCl_3$–MeOH (5:2), B] to give ikarisoside C (**3**, 20 mg, 0.12%).

Isolation of flavonol glycosides from the root of E. sempervirens. The roots of *E. sempervirens* (fr. wt 1.6 kg) were exhaustively extracted with MeOH within 15 hr after collection. Evaporation of the soln to dryness yielded 74.7 g of residue. The MeOH extract was chromatographed on deactivated silica gel (300 g) using $C_6H_6(H_2O)$–MeOH (1:0 → 1:1) as eluent, each fraction (eluted vol. 500 ml) being monitored by TLC. Fractions 41–44 eluted with $C_6H_6(H_2O)$–MeOH (9:1) and 45 and 46 with $C_6H_6(H_2O)$–MeOH (4:1) were evapd to give 4.7 g of residue. After the MeOH soln of the residue was allowed to stand, the yellow ppt. was collected. and recryst. from MeOH to give ikarisoside A (**1**, 310 mg, 2×10^{-2}%). The mother liquor was purified on a Sephadex LH-20 column using Me_2CO and by prep. TLC [$CHCl_3$–MeOH (5:1), A], sequentially, to give ikarisoside E (**5**, 28 mg, 1.7×10^{-3}%) and icarisid II (**9**, 50 mg, 3×10^{-3}%). Fraction 49 eluted with $C_6H_6(H_2O)$–H_2O (4:1) and fraction 50 with $C_6H_6(H_2O)$–MeOH (1:1) were evapd to give 7.3 g of residue, a part of which (1.5 g) was purified by prep. TLC [$CHCl_3$–MeOH (5:1), B, A] to give icariin (**10**, 50 mg, 1.5×10^{-2}%) amd epimedoside A (**8**, 9 mg, 2.8×10^{-5}%). Fraction 51 eluted with $C_6H_6(H_2O)$–MeOH (1:1) was evapd to give 43 g of residue, a part of which (2.2 g) was purified by prep. TLC [$CHCl_3$–MeOH (5:2), B, C; $CHCl_3$–MeOH (4:1), A] to give ikarisoside C (**3**, 90 mg, 0.11%).

Ikarisoside A (**1**). Compound **1** was recryst. from Me_2CO to give yellow needles, mp 152–154°, and from MeOH-H_2O to give needles, mp 160°, indentical with lit. [6] value (mp 153–155°). $[\alpha]_D^{16}$-79° (C_5H_5N; *c* 0.99). $FeCl_3$ test: dark brown, Mg–HCl test: positive, Zn–HCl test: positive, $ZrOCl_2$–citric acid test: negative, $ZrOCl_2$–citric acid–HCl test: positive, Gibbs test: negative. EIMS (probe) 20 eV, *m/z* (rel. int.): 501 $[M+1]^+$ (0.6), 500 $[M]^+$ (3), 370 (6), 355 (42), 354 (100), 339 (76), 337 (6), 299 (48), 286 (50), 147 (1), 128 (15), 121 (8); 75 eV, *m/z* (rel. int.): 370 (2), 355 (31), 354 (93), 339 (100), 337 (8), 325 (7), 311 (11), 299 (86), 286 (74), 270 (10), 233 (3), 165 (24), 128 (16), 121 (54), 69 (18). UV λ_{max}^{EtOH} nm (log ε): 224 (sh 4.36), 271 (4.33), 310 (4.10), 354 (sh 4.03); $\lambda_{max}^{EtOH+AlCl_3}$ 224 (sh 4.35), 274 (4.33), 310 (sh 4.10), 345 (4.17); $\lambda_{max}^{EtOH+NaOAc}$ 278 (4.66), 310 (sh 4.50), 350 (4.36). ^1H NMR (DMSO-d_6, 50°): δ0.83 (3H, *d*, *J* = 6 Hz, Me-5″), 1.63 and 1.69 (6H, *br s*, 2 × Me-11), 3.18 (2H, *m*, H-4″ and H-5″), 3.36 and 3.43 (2H, *br dd*, *J* = 7 and 14 Hz, 2 × H-9), 3.51 (1H, *br dd*, *J* = *ca* 4 and 8 Hz, H-3″), 4.01 (1H, *br*, H-2″), 5.17 (1H, *q t*, *J* = 1 and 7 Hz, H-10), 5.30 (1H, *d*, *J* = 1.5 Hz, H-1″), 6.32 (1H, *s*, H-6), 6.93 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.77 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.54 (1H, *s*, OH-5), 4.46, 4.60, 4.84. 10.02 and 10.08 (5H, *br s*, 5 × OH), the proton signals of the rhamnosyl moiety were assigned by decoupling experiments ^1H NMR (C_5D_5N, 23°): δ1.47 (3H, *d*, *J* = 6 Hz, Me-5″), 1.67 and 1.85 (6H, *br s*, 2 × CH_3-11), 3.79 and 3.84 (2H, *br dd*, *J* = 7 and 15 Hz, 2 × H-9), 4.25 (1H, *qd*, *J* = 6 and 9.5 Hz, H-5″), 4.33(1H, *dd*, *J* = 9 and 9.5 Hz, H-4″), 4.66 (1H, *dd*, *J* = 3.5 and 9 Hz, H-3″), 5.14 (1H, *dd*, *J* = 1.5 and 3.5 Hz, H-2″), 5.62 (1H, *br t*, *J* = 7 Hz, H-10), 6.33 (1H, *d*, *J* = 1.5 Hz, H-1″), 6.78 (1H, *s*, H-6), 7.35 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 8.22 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 13.36 (1H, *s*, OH-5), the proton signals of the rhamnosyl moiety were assigned by decoupling expt. The ^{13}C NMR spectrum is described in Table 1.

Ikarisoside B (**2**). The compound (**2**) was obtained as a yellow amorphous powder. $[\alpha]_D^{22}$-78° (MeOH; *c* 0.19). $FeCl_3$ test: green, Mg–HCl test: positive, Zn–HCl test: positive, $ZrOCl_2$–citric acid test: negative, $ZrOCl_2$–citric acid–HCl test: positive, Gibbs test: negative. FABMS *m/z* (rel. int.): 685 $[M+Na]^+$ (3), 663 $[M+H]^+$ (2), 501 [M + H-glucosyl + H]$^+$ (2), 483 (2), 355 [M + H-glucosyl + H − rhamnosyl + H]$^+$ (100), 339 (31), 299 (57), 165 (18), 121 (46). UV λ_{max}^{MeOH} nm (log ε): 206 (4.32), 222 (3.95), 269 (3.97), 310 (3.62), 350 (3.57); $\lambda_{max}^{MeOH+AlCl_3}$ 206 (4.34), 230 (3.89), 278 (3.93), 305 (3.67), 345 (3.75), 405 (3.57); $\lambda_{max}^{MeOH+NaOAc}$ 206 (4.54), 271 (3.97), 310 (sh 3.62), 355 (3.57); $\lambda_{max}^{MeOH+NaOMe}$ 204 (4.42), 277 (4.02), 328 (3.62), 392 (3.80). ^1H NMR (DMSO-d_6, 50°): δ0.89 (3H, *d*, *J* = 6 Hz, Me-5″), 1.63 and 1.69 (6H, *br s*, 2 × Me-11), *ca* 3.05 (2H, *m*) *ca* 3.1–3.4 (3H, *m*), 3.17 (1H, *t*, *J* = 9 Hz, H-4″, overlapping with other signals), 3.32 (1H, *m*, H-5″, overlapping with other signals), 3.49 (1H, *br d*-like, *J* = 3.5 *Hz*), 3.58 (1H, *dd*, *J* = 3 and 9 Hz, H-3″), 4.12 (1H, *dd*, *J* = 1.5 and 3 Hz, H-2″), 4.29 (1H, *d*, *J* = 8 Hz, H-1‴), 5.17 (1H, *br t*, *J* = 7 Hz, H-10), 5.58 (1H, *br s*, H-1″), 6.33 (1H, *s*, H-6), 6.95 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.78 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.44 (1H, *s*, OH-5), the proton signals of the rhamnosyl moiety were assigned by decoupling expt. ^1H NMR (C_5D_5N, 23°): δ1.43 (3H, *d*, *J* = 6 Hz, Me-5″), 1.67 and 1.84 (6H, *br s*, 2 × Me-11), 3.79 (3H, *br d*-like, *J* = 7 Hz, 2 × H-9), 3.95 (1H, *m*), 4.09 (1H, *m*), 4.22 (1H, *t*, *J* = 9.5 Hz, H-4″), *ca* 4.2–4.35 (1H, *m*), 4.31 (1H, *qd*, *J* = 6 and 9.5 Hz, H-5″, overlapping with other signal), 4.42 (1H, *dd*, *J* = 4.5 and 12 Hz), 4.48 (1H, *dd*, *J* = 2 and 12 Hz), 4.65 (1H, *dd*, *J* = 3 and 9.5 Hz, H-3″), 5.09 (1H, *br*, H-2″), 5.28 (1H, *d*, *J* = 7 Hz, H-1‴), 5.60 (1H, *br t*, *J* = 7 Hz, H-10), 6.36 (1H, *br s*, H-1″), 6.81 (1H, *s*, H-6), 7.37 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 8.14 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.30 (1H, *s*, OH-5), the proton signals of the rhamnosyl moiety were assigned by decoupling expt. ^{13}C NMR spectrum is described in Table 1.

Ikarisoside C (**3**). The coupound (**3**) was obtained as a yellow amorphous powder. $[\alpha]_D^{22}$-72° (MeOH; *c* 0.37). $FeCl_3$ test: green, Mg-HCl test: positive, Zn–HCl test: positive, $ZrOCl_2$–citric acid test: negative, $ZrOCl_2$–citric acid–HCl test: positive, Gibbs test: negative. FABMS *m/z* (rel. int.): 847 $[M+Na]^+$ (32), 825 $[M+H]^+$ (21), 663 [M + H − glucosyl + H]$^+$ (18), 517 [M + H − glucosyl + rhamnosyl + H]$^+$ (100), 355 [M + H − glucosyl + H − rhamnosyl + H]$^+$ (36), 339 (18), 299 (36). UV λ_{max}^{MeOH} nm (log ε): 204 (4.52), 240 (4.22), 269 (4.28), 320 (4.00), 350 (3.96); $\lambda_{max}^{MeOH+AlCl_3}$ 206 (4.26), 235 (4.17), 277 (4.26), 305 (3.95), 345 (4.08), 405 (3.87); $\lambda_{max}^{MeOH+NaOAc}$ 208 (4.69), 269 (4.28), 320 (3.95), 355 (3.97); $\lambda_{max}^{MeOH+NaOMe}$ 210 (4.81), 242 (4.21), 270 (4.22), 298 (3.99), 345 (sh 4.04), 385 (4.13). ^1H NMR (DMSO-d_6, 50°): δ0.88 (3H, *d*, *J* = 6 Hz, Me-5″), 1.61 and 1.69 (6H, *br s*, 2 × Me-11), *ca* 2.98–3.08 (2H, *m*), *ca* 3.16–3.60 (*m*, the amount of protons could not be defined), 3.15 (1H, *m*, H-4″), 3.35 (1H, *m*, H-3″), *ca* 3.35 (2H, *m*, 2 × H-9, assigned by decoupling expt), 3.36 (1H, *m*, H-5″), 4.13 (1H, *dd*, *J* = 1 and 3 Hz, H-2″), 4.28 (1H, *d*, *J* = 8 Hz, H-1‴), 4.99 (1H, *d*, *J* = 7 Hz, H-1⁗), 5.19 (1H, *br t*, *J* = 7 Hz, H-10), 5.56 (1H, *d*, *J* = 1 Hz, H-1″), 6.62 (1H, *s*, H-6), 6.96 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.81 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.51 (1H, *br s*, OH-5), the proton signals of the rhamnosyl moiety were assigned by decoupling expt, the signals at 3.35–3.36 were overlapping with other signals. ^1H NMR (C_5H_5N, 23°): δ1.45 (3H, *d*, *J* = 6 Hz, Me-5″), 1.58 and 1.76 (6H, *br s*, 2 × Me-11), *ca* 3.70 (2H, *m*), *ca* 3.84 (2H, *m*), 3.96 (1H, *m*), 4.09 (1H, *dd*, *J* = 8 and 9 Hz), 4.14 (1H, *m*), 4.21 (1H, *t*, *J* = 9 Hz), *ca* 4.28 (2H, *m*), *ca* 4.3–4.4 (2H, *m*), 4.48 (1H, *m*), 4.53 (1H, *m*), 4.62 (1H, *dd*, *J* = 3 and 9 Hz, H-3″), 5.09 (1H, *br*, H-2″), 5.30 (1H, *d*, *J* = 8 Hz, H-1‴), 5.56 (1H, *br t*, *J* = 7 Hz, H-10), 5.75 (1H, *br d*, *J* = 8 Hz, H-1⁗), 6.32 (1H, *br s*, H-1″), 7.34 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 8.12 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′). ^{13}C NMR spectrum is described in Table 1).

Ikarisoside D (**4**). The compound (**4**) was obtained as a yellow amorphous powder. $[\alpha]_D^{27}$-64° (MeOH; *c* 0.097). $FeCl_3$ test: green, Mg–HCl test: positive, Zn–HCl test: positive, $ZrOCl_2$–citric acid test: negative, $ZrOCl_2$–citric acid–HCl test: positive, Gibbs test: negative, EIMS (probe) 70 eV, *m/z* (rel. int.): 542 $[M]^+$ (11), 446 (38), 396 (72), 370 (14), 354 (> 100). FABMS *m/z* (rel. int.): 565 $[M+Na]^+$ (12), 543 $[M+H]^+$ (2), 355 (84), 339 (28), 299 (67), 283 (15), 165 (22), 121 (84), 69 (100), 43 (> 100). UV λ_{max}^{MeOH} nm (log ε): 210 (4.52), 220 (sh 4.43), 269 (4.45), 310 (4.17), 350 (sh 4.12); $\lambda_{max}^{MeOH+AlCl_3}$ 210 (4.56), 230 (sh 4.38), 278 (4.42), 306 (4.18), 345 (4.21); $\lambda_{max}^{MeOH+NaOAc}$ 210 (4.57), 222 (sh 4.45), 270 (4.44), 310 (sh 4.13), 350 (sh 4.07); $\lambda_{max}^{MeOH+NaOMe}$ 210 (4.67), 230 (sh 4.43), 278 (4.51), 327 (4.20), 405 (4.34). ^1H NMR (DMSO-d_6, 23°): δ0.72 (3H, *d*, *J* = 6 Hz, Me-5″), 1.63 and 1.68 (6H, *br s*, 2 × Me-11), 2.00 (3H, *s*, OAc), 3.32 (1H, *qd*, *J* = 6 and 10 Hz, H-5′), 3.35 and 3.41 (2H, *br dd*, *J* = 7 and 10 Hz, 2 × H-9), 3.73 (1H, *dd*, *J* = 3 and 9 Hz, H-3″), 4.05 (1H, *dd*, *J* = 1.5 and 3 Hz, H-2″), 4.71 (1H, *dd*, *J* = 9 and 10 Hz, H-4″), 5.18 (1H, *br t*, *J* = 7 Hz, H-10), 5.31 (1H, *d*, *J* = 1.5 Hz, H-1″), 6.33 (1H, *s*, H-6), 6.96 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.74 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.49 (1H, *s*, OH-5), the proton signals of the rhamnosyl moiety were assigned by decoupling expt. The ^{13}C NMR spectrum is described in Table 1.

Ikarisoside E (**5**). The compound (**5**) was obtained as a yellow amorphous powder. $[\alpha]_D^{22}$-92° (MeOH; *c* 0.18). $FeCl_3$ test: green, Mg–HCl test: positive, $ZrOCl_2$–citric acid test: negative, $ZrOCl_2$–citric acid–HCl test: positive, Gibbs test: negative. EIMS (probe) 30 eV, *m/z* (rel. int.): 498 $[M]^+$ (20), 352 (35), 338 (34), 337 (100), 75 eV, *m/z* (rel. int.): 376 (6), 353 (10), 352 (40), 338 (28), 337 (100), 203 (16), 164 (23). UV λ_{max}^{MeOH} nm (log *ε*): 205 (4.26), 227 (4.38), 275 (4.41), 305 (4.14), 317 (sh 4.11), 370 (sh 3.80); $\lambda_{max}^{MeOH+AlCl_3}$ 205 (4.64), 228 (4.35), 243 (sh 4.28), 282 (4.42), 317 (4.10), 350 (4.13), 420 (3.73); $\lambda_{max}^{MeOH+NaOAc}$ 207 (4.93), 230 (sh 4.40), 275 (4.41), 305 (4.11), 318 (4.07), 365 (3.85); $\lambda_{max}^{MeOH+NaOMe}$ 210 (5.09), 280 (4.41), 302 (sh 4.32), 345 (4.11), 395 (4.08). ^1H NMR (DMSO-d_6, 50°): δ0.85 (3H, *d*, *J* = 6 Hz, Me-5‴), 1.43 and 1.44 (6H, *s*, 2 × Me-6″), 3.20 (2H, *m*, H-4‴ and H-5‴), 3.53 (1H, *dd*, *J* = 2 and 9 Hz, H-3‴), 4.01 (1H, *br dd*-like, H-2‴), 5.33 (1H, *d*, *J* = 1 Hz, H-1‴), 5.73 (1H, *d*, *J* = 10 Hz, H-5″), 6.21 (1H, *s*, H-6), 6.73 (1H, *d*, *J* = 10 Hz, H-4″), 6.91 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.80 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.54 (1H, *br s*, OH-5). ^1H NMR (CD_3OD, 23°): δ0.96 (3H, *d*, *J* = 6 Hz, Me-5‴), 1.44 and 1.45 (6H, *s*, 2 × Me-6″), *ca* 3.3–3.4 (2H, *m*, H-4‴ and H-5‴), 3.77 (1H, *dd*, *J* = 3 and 10 Hz, H-3‴), 4.24 (1H, *dd*, *J* = 1.5 and 3 Hz, H-2‴), 5.38 (1H, *d*, *J* = 1.5 Hz, H-1‴), 5.67 (1H, *d*, *J* = 10 Hz, H-5″), 6.14 (1H, *s*, H-6), 6.71 (1H, *d*, *J* = 10 Hz, H-4″), 6.89 (2H, *d*, *J* = 9 Hz, H-3′ and H-4′), 7.77 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′). The ^{13}C NMR spectrum is described in Table 1.

Ikarisoside F (**6**). The compound (**6**) was recryst. from EtOAc to give pale yellow needles, mp 174–179° and from MeOH to give pale yellow needles, mp 178–179°. $[\alpha]_D^{22}$-67° (MeOH; *c* 0.20). $FeCl_3$ test: green, Mg–HCl test: positive, Zn–HCl test: positive, $ZrOCl_2$–citric acid test: negative, $ZrOCl_2$–citric acid–HCl test: positive, Gibbs test: negative. FABMS *m/z* (rel. int.): 633 $[M+H]^+$ (19), 501 $[M+H-xylosyl+H]^+$ (5), 483 (4), 355 $[M+H-xylosyl+H-rhamnosyl+H]^+$ (> 100), 339 (59), 299 (98), 165 (37), 121 (100). UV λ_{max}^{MeOH} nm (log *ε*): 206 (4.28), 220 (sh 4.14), 269 (4.17), 310 (3.89), 350 (sh 3.83); $\lambda_{max}^{MeOH+AlCl_3}$ 206 (4.34), 230 (4.10), 277 (4.12), 305 (3.91), 344 (3.92), 410 (3.61); $\lambda_{max}^{MeOH+NaOAc}$ 206 (4.38), 220 (sh 4.17), 269 (4.17), 310 (sh 3.86), 350 (sh 3.83); $\lambda_{max}^{MeOH+NaOMe}$ 225 (sh 4.16), 278 (4.25), 325 (3.94), 392 (4.07). ^1H NMR (DMSO-d_6, 50°): δ0.90 (3H, *d*, *J* = 6 Hz, Me-5‴), 1.62 and 1.68 (6H, *br s*, 2 × Me-11), *ca* 2.94–3.02 (2H, *m*), 3.08 (1H, *t*, *J* = 9 Hz), 3.14 (1H, *dd*, *J* = 9 and 10 Hz, H-4″), 3.23 (1H, *m*), 3.34 (1H, *br d*), *ca* 3.4 (2H, *m*), 3.45 (1H, *qd*, *J* = 6 and 10 Hz, H-5″), 3.55 (1H, *dd*, *J* = 6 and 10 Hz), 3.58 (1H, *dd*, *J* = 3 and 9 Hz, H-3″), 4.05 (1H, *dd*, *J* = 1.5 and 3 Hz, H-2″), 4.22 (1H, *d*, *J* = 7.5 Hz, H-1‴), 5.16 (1H, *br t*, *J* = 7 Hz, H-10), 5.37 (1H, *d*, *J* = 1.5 Hz, H-1″), 6.28 (1H, *s*, H-6), 6.94 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.76 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.55 (1H, *s*, OH-5), the proton signals of the rhamnosyl moiety were assigned by decoupling expt. The signals at δ3.25–3.45 overlapped with those of H_2O and hydroxyl groups. ^1H NMR (C_5D_5N, 23°): δ1.44 (3H, *d*, *J* = 6 Hz, Me-5′), 1.67 and 1.84 (6H, *br s*, 2 × Me-11), 3.71 (1H, *br m*), 3.81 (2H, *br d*, *J* = 7 Hz, 2 × H-9), 4.05 (1H, *br t*-like), *ca* 4.14 (2H, *m*), 4.21 (1H, *t*, *J* = 9.5 Hz, H-4″), 4.32 (1H, *br dd*, *J* = 5 and 11 Hz), 4.44 (1H, *qd*, *J* = 6 and 9.5 Hz, H-5″), 4.68 (1H, *dd*, *J* = 3 and 9.5 Hz, H-3″), 5.05 (1H, *br d*, *J* = 3 Hz, H-2″), 5.20 (1H, *d*, *J* = 7.5 Hz, H-1‴), 5.62 (1H, *br t*, *J* = 7 Hz, H-10), 6.35 (1H, *br s*, H-1″), 6.77 (1H, *s*, H-6), 7.35 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 8.17 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 13.39 (1H, *br s*, OH-5). The ^{13}C NMR spectrum is described in Table 1.

Epimedoside A (**8**). Compound **8** was recryst. from MeOH to give yellow prisms, mp 212–213° (lit. [6] value, 191–192°, yellow needles). FABMS *m/z* (rel. int.): 685 $[M+Na]^+$ (4), 663 $[M+H]^+$ (14), 517 $[M-rhamnosyl+H]^+$ (48), 501 $[M-glucosyl+H]^+$ (9), 355 $[M-glucosyl+H-rhamnosyl+H]^+$ (100), 339 (26), 299 (23). ^1H NMR (DMSO-d_6, 50°): δ0.82 (3H, *d*, *J* = 6 Hz, Me-5‴), 1.61 and 1.69 (6H, *br s*, 2 × Me-11), *ca* 3.1–3.9 (11H, *m*), 4.01 (1H, *br s*, H-2″), 5.00 (1H, *d*, *J* = 9 Hz, H-1‴), 5.31 (1H, *d*, *J* = 1.5 Hz, H-1″), 6.63 (1H, *s*, H-6), 6.94 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.80 (1H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.56 (1H, *s*, OH-5). The ^{13}C NMR spectrum is described in Table 1.

Icarisid II (**9**). Compound **9** was cryst. from pyridine + H_2O to give yellow needles, mp 204–206°, identical with lit. [1] value (203–205°). $[\alpha]_D^{16}$-121° (MeOH; *c* 0.089). $FeCl_3$ test: green, Mg–HCl test: positive, Zn–HCl test: positive, $ZrOCl_2$–citric acid test: negative, $ZrOCl_2$–citric acid–HCl test: positive. EIMS (probe) 30 eV, *m/z* (rel. int.): 514 $[M]^+$ (2), 369 (33), 368 (100), 353 (57), 352 (12), 351 (13), 315 (26), 313 (20), 300 (28). UV λ_{max}^{EtOH} nm (log *ε*): 224 (sh 4.27), 271 (4.30), 298 (4.03), 350 (sh 3.89); $\lambda_{max}^{EtOH+AlCl_3}$ 228 (sh 4.24), 277 (4.22), 307 (4.05), 340 (4.01), 395 (sh 3.61); $\lambda_{max}^{EtOH+NaOMe}$ 282 (4.41), 385 (3.84); $\lambda_{max}^{EtOH+NaOAc}$ 271 (4.30), 310 (sh 4.01), 350 (sh 3.88). ^1H NMR (DMSO-d_6, 23°): δ0.79 (3H, *d*, *J* = 6 Hz, Me-5‴), 1.63 and 1.68 (6H, *br s*, 2 × Me-11), 3.03 (1H, *qd*, *J* = 6 and 9.5 Hz, H-5″), 3.14 (1H, *dd*, *J* = 9 and 9.5 Hz, H-4″), *ca* 3.4 (2H-9, overlaping with the signals of H_2O), 3.47 (1H, *br*, H-3″), 3.85 (3H, *s*, OMe-4′), 3.98 (1H, *br*, H-2″), 5.15 (1H, *br t*, *J* = 7 Hz, H-10), 5.26 (1H, *d*, *J* = 1.5 Hz, H-1″), 6.31 (1H, *s*, H-6), 7.12 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.86 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.52 (1H, *s*, OH-5).

Icariin (**10**). Compound **10** was recryst. from pyridine + H_2O to give yellow needles, mp 266–229°, identical with lit. [7] value (225–227°). $FeCl_3$ test: green, $ZrOCl_2$–citric acid test: negative, $ZrOCl_2$–citric acid–HCl test: positive. FABMS *m/z* (rel. int.): 677 $[M+H]^+$ (11), 531 $[M+H-rhamnosyl+H]^+$ (84), 515 $[M+H-glucosyl+H]^+$ (10), 369 $[M+H-glucosyl+H-rhamnosyl+H]^+$ (84), 353 (20). UV λ_{max}^{EtOH} nm (log *ε*): 224 (sh 4.39), 271 (4.36), 314 (4.17), 350 (sh 3.97); $\lambda_{max}^{EtOH+AlCl_3}$ 230 (sh 4.34), 281 (4.34), 306 (4.17), 340 (4.17), 408 (3.78); $\lambda_{max}^{EtOH+NaOAc}$ 271 (4.36), 314 (4.17), 350 (sh 3.97); $\lambda_{max}^{EtOH+NaOMe}$ 285 (4.37), 305 (sh 4.25), 382 (3.96). ^1H NMR (DMSO-d_6, 50°): δ0.81 (3H, *d*, *J* = 6 Hz, Me-5‴), 1.61 and 1.69 (6H, *br s*, 2 × Me-11), *ca* 3.1–3.3 (*m*), 3.33 (1H, *br d*-like, *J* = *ca* 5 Hz), *ca* 3.4–3.6 (*m*), *ca* 3.7–3.76 (1H, *m*), 3.86 (3H, *s*, OMe-4′), 4.01 (1H, *br*, H-2″), 5.00 (1H, *d*, *J* = 7.5 Hz, H-1‴), 5.19 (1H, *br t*, *J* = 7 Hz, 10-H), 5.30 (1H, *d*, *J* = 1.5 Hz, H-1″), 6.64 (1H, *s*, H-6), 7.12 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.89 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), 12.53 (1H, *s*, OH-5).

Ikarisoside A peracetate (**1a**). A mixture of **1** (20 mg), Ac_2O (1 ml) and pyridine (1 ml) was kept at room temp. for 48 hr, and then poured into ice-water. The solid was collected and purified by prep. TLC [$CHCl_3$–Me_2CO (10:1); A] to give an amorphous powder (**1a**). $FeCl_3$ test: negative. FABMS *m/z* (rel. int.): 775 $[M$

+ Na]$^+$ (8), 753 [M + H]$^+$ (25), 711 (10), 505 (8), 481 (51), 439 (> 100), 397 (100), 395 (> 100), 354 (79), 341 (78). ^{1}H NMR (DMSO-d_6, 50°): δ0.79 (3H, *d*, *J* = 6 Hz, Me-5″), 1.63 and 1.65 (6H, *br s*, 2 × Me-11), 1.95, 1.98, 2.09, 2.31, 2.33 and 2.35 (18H, *s*, 6 × OAc), 3.29 (1H, *qd*, *J* = 6 and 10 Hz, H-5″), 3.46 and 3.55 (2H, *br dd*, *J* = 7 and 15 Hz, 2 × H-9), 4.79 (1H, *t*, *J* = 10 Hz, H-4″), 5.10 (1H, *dd*, *J* = 3.5 and 10 Hz, H-3″), 5.12 (1H, *br t*, *J* = 7 Hz, H-10), 5.40 (1H, *d*, *J* = 2 Hz, H-1″), 5.52 (1H, *dd*, *J* = 2 and 3.5 Hz, H-2″), 7.10 (1H, *s*, H-6), 7.38 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.95 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), the proton signals of the rhamnosyl moiety were assigned by decoupling expt.

Ikarisoside B peracetate (**2a**). A mixture of **2** (115 mg). Ac_2O (1.5 ml) and pyridine (0.5 ml) was kept at room temp. for 96 hr, and worked-up in the usual manner. The product was purified by prep. TLC [$CHCl_3$-Me_2CO (6:1); A] to give an amorphous powder (**2a**, 80 mg). $FeCl_3$ test: negative. FABMS *m/z* (rel. int.): 1040 [M]$^+$ (14), 693 (66), 651 (38), 609 (21), 561 (> 100), 519 (41), 481 (75), 439 (100), 395 (85), 354 (90). ^{1}H NMR (DMSO-d_6, 50°): δ0.73 (3H, *s*, *J* = 6 Hz, Me-5″), 1.62 and 1.64 (6H, *br s*, 2 × Me-11), 1.938, 1.941, 1.96, 1.97, 2.01, 2.05, 2.31, 2.32 and 2.35 (27H, *s*, 9 × OAc), 3.16 (1H, *qd*, *J* = 6 and 10 Hz, H-5″), 3.45 and 3.54 (2H, *br dd*, *J* = 7 and 15 Hz, 2 × H-9), 3.99 (2H, *m*), 4.30 (1H, *dd*, *J* = 5 and 12 Hz), 4.35 (1H, *dd* *J* = 1 and 3 Hz, H-2″), 4.67 (1H, *t*, *J* = 10 Hz, H-4″), 4.79 (1H, *dd*, *J* = 8 and 10 Hz, H-2‴), 4.87 (1H, *d*, *J* = 8 Hz, H-1‴), 4.93 (1H, *t*, *J* = 10 Hz), 5.09 (1H, *dd*, *J* = 3 and 10 Hz, H-3″), 5.12 (1H, *br t*, *J* = 7 Hz, H-10), 5.27 (1H, *t*, *J* = 10 Hz), 5.52 (1H, *d*, *J* = 1 Hz, H-1″), 7.09 (1H, *s*, H-6), 7.37 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-5′), 7.93 (2H, *d*, *J* = 8.5 Hz, H-2′ and H-6′), the proton signals of the rhamnosyl moiety were assigned by decoupling expt.

Ikarisoside C peracetate (**3a**). A mixture of **3** (19 mg), Ac_2O (1 ml) and pyridine (1 ml) was kept at room temp. for 120 hr, and treated as usual. The product was purified by prep. TLC [$CHCl_3$–Me_2CO (6:1); A] to give an amorphous powder (**3a**). $FeCl_3$ test: negative. FABMS *m/z* (rel. int.): 1329 [M + H]$^+$ (29), 1287 (8), 1245 (8), 999 (8), 769 (80), 651 (75), 609 (38), 561 (> 100), 519 (100). ^{1}H NMR (DMSO-d_6, 50°): δ0.71 (3H, *d*, *J* = 6 Hz, Me-5″), 1.61 (6H, *br s*, 2 × Me-11), 1.93, 1.94, 1.96, 1.97, 1.98, 2.00, 2.01, 2.04, 2.30 and 2.32 (30H, *s*, 10 × OAc), 2.02 (6H, *s*, 2 × OAc), 3.12 (1H, *qd*, *J* = 6 and 10 Hz, H-5″), 3.41 and 3.49 (2H, *br dd*, *J* = 7 and 14 Hz, 2 × H-9), *ca* 3.9–4.03 (2H, *m*), *ca* 4.1–4.2 (2H, *m*), *ca* 4.25–4.35 (2H, *m*) 4.35 (1H, *dd*, *J* = 1.5 and 3 Hz, H-2″), 4.66 (1H, *t*, *J* = 10 Hz, H-4″), 4.79 (1H, *dd*, *J* = 9 and 10 Hz), 4.87 (1H, *d*, *J* = 8 Hz, H-1‴), 4.93 (1H, *t*, *J* = 10 Hz), 5.02 (1H, *t*, *J* = 10 Hz), 5.07 (1H, H-10, overlapping with the signal of H-3″), 5.07 (1H, *dd*, *J* = 3 and 10 Hz, H-3″), 5.18 (1H, *dd*, *J* = 8 and 10 Hz), 5.27 (1H, *t*, *J* = 10 Hz), 5.40 (1H, *t*, *J* = 10 Hz), 5.51 (1H, *d*, *J* = 1.5 Hz, H-1″), 5.74 (1H, *d*, *J* = 9 Hz, H-1⁗), 6.97 (1H, *s*, H-6), 7.36 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.91 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), the proton signals of the rhamnosyl moiety were assigned by decoupling expt.

Ikarisoside E peracetate (**5a**). A mixture of **5** (16 mg), Ac_2O (1 ml) and pyridine (1 ml) was kept at room temp. for 96 hr, and treated as usual. The product was purified by prep. TLC [$CHCl_3$–EtOAc (7:1); A] to give an amorphous powder (**5a**, 15 mg). $FeCl_3$ test: negative. FABMS *m/z* (rel. int.): 709 [M + H]$^+$ (5), 437 (6), 395 (24), 273 (56), 213 (8), 171 (22), 153 (72), 111 (79), 43 (100). ^{1}H NMR (DMSO-d_6, 50°): δ0.77 (3H, *d*, *J* = 6 Hz, Me-5‴), 1.47 and 1.49 (6H, *s*, 2 × Me-6″), 1.95, 1.97, 2.09, 2.30 and 2.31 (15H, *s*, 5 × OAc), 3.27 (1H, *qd*, *J* = 6 and 10 Hz, H-5‴), 4.78 (1H, *t*, *J* = 10 Hz, H-4‴), 5.09 (1H, *dd*, *J* = 3 and 10 Hz, H-3‴), 5.39 (1H, *d*, *J* = 2 Hz, H-1‴), 5.51 (1H, *dd*, *J* = 2 and 3 Hz, H-2‴), 5.92 (1H, *d*, *J* = 10 Hz, H-5″), 6.55 (1H, *d*, *J* = 0.8 Hz, H-6), 6.81 (1H, *dd*, *J* = 0.8 and 10 Hz, H-4″), 7.35 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.97 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′).

Ikarisoside F peracetate (**6a**). A mixture of **6** (18 mg), Ac_2O (1 ml) and pyridine (1 ml) was kept at room temp. for 48 hr, and treated as usual. The product was purified by prep. TLC ($CHCl_3$–Me_2CO (10:1); A] to give an amorphous powder (**6a**). $FeCl_3$ test: negative. FABMS *m/z* (rel. int.): 991 [M + Na]$^+$ (38), 969 [M + H]$^+$ (> 100), 927 (13), 711 (45), 693 (100), 651 (73). ^{1}H NMR (DMSO-d_6, 50°): δ0.77 (3H, *d*, *J* = 7 Hz, Me-5‴), 1.63 and 1.65 (6H, *br s*, 2 × Me-11), 1.96, 1.97, 2.00, 2.01, 2.05, 2.30, 2.34 and 2.49 (24H, *s*, 8 × OAc), 3.43 (1H, *qd*, *J* = 6 and 10 Hz, H-5″), *ca* 3.4–3.55 (3H, *br m*), 3.88 (1H, *dd*, *J* = 5 and 11.5 Hz), 4.31 (1H, *br dd*, *J* = *ca* 1 and 3 Hz, H-2″), 4.70 (1H, *t*, *J* = 10 Hz, H-4″), *ca* 4.7–4.85 (3H, *m*), 5.11 (1H, *dd*, *J* = 3 and 10 Hz, H-3″), 5.15 (1H, *t*, *J* = 9 Hz), 5.28 (1H, *br d*, *J* = *ca* 1 Hz, H-1″), 7.10 (1H, *s*, H-6), 7.37 (2H, *d*, *J* = 9 Hz, H-3′ and H-5′), 7.93 (2H, *d*, *J* = 9 Hz, H-2′ and H-6′), the proton signals of the rhamnosyl moiety were assigned by decoupling expt.

Formation of ikarisoside E (**5**) *from ikarisodide A* (**1**). A mixture of **1** (20 mg) and $PdCl_2$ (2 mg) in 90% aq. MeOH soln (1 ml) was kept at room temp. for 16 hr. The product was purified by prep. TLC [$CHCl_3$–MeOH (5:1); A] to give an amorphous powder (**5′**, 7.5 mg). The IR, ^{1}H NMR and ^{13}C NMR spectra of **5′** were in agreement with those of **5**, respectively.

Acknowledgements—We are grateful to Dr. K. Suzuki, Tokyo Metropolitan University and Dr. N. Sahashi, Toho University, for valuable advice on the identification of the materials.

REFERENCES

1. Akai, S. (1935) *Yakugaku Zasshi* **55**, 537.
2. Akai, S., Imaida, M. and Matsukawa, T. (1935) *Yakugaku Zasshi* **55**, 1139.
3. Tomita, M. and Ishii, H. (1957) *Yakugaku Zasshi* **77**, 212.
4. Matsuura, S., Yamazaki, F., Hirose, K., Maeda, E. and Mizuno, M. (1971) *Syoyakugaku Zasshi* **25**, 122.
5. Fujita, M., Itokawa, H. and Koyama, M. (1971) *Tokyo Yakka Daigaku Nempo* **21**, 50.
6. Takemoto, T., Daigo, K. and Tokuoka, Y. (1975) *Yakugaku Zasshi* **95**, 312.
7. Tokuoka, Y., Daigo, K. and Takemoto, T. (1975) *Yakugaku Zasshi* **95**, 825.
8. Itoh, Y., Hirayama, S., Sudo, K., Ojima, M., Sagara, K. and Yoshida, T. (1986) Abstracts of the papers of the 15th Symposium on the Analytical Chemistry of Crude Drugs (Dai 15kai Shyouyaku Bunseki Touronkai Youshisyu), Kobe (Japan), p. 29.
9. Mizuno, M., Hanioka, S., Suzuki, N., Iinuma, M., Tanaka, T., Xin-Shun, L. and Zhi-da, M. (1987) *Phytochemistry* **26**, 861.
10. Kohno, H., Takaba, K., Fukai, T. and Nomura, T. (1987) *Heterocycles* **26**, 759.
11. Hörhammer, L. and Hänsel, R. (1953) *Arch. Pharm. Ber. Dtsch. Pharm. Ges.* **286**, 425.
12. Okamoto, T. and Murakami, T. (1970) *Tennenbutsu kagaku* (*Chemistry of Natural Products*) p. 249. Hirokawa Shoten, Tokyo.
13. Markham, K. R., Chari, V. M. and Mabry., T. J. (1982) in *The Flavonoids, Advances in Research* (Harborne, J. B. and Mabry, T. J., eds) Chap. 2. Chapman & Hall, London.
14. Bock, K., Lundt, I. and Pedersen C. (1973) *Tetrahedron Letters* 1037.
15. Liptak, A., Nánási, P., Neszmélyi, A. and Wagner, H. (1980) *Tetrahedron* **36**, 1261.
16. Kasai, R., Okihara, M., Asakawa, J., Mizutani, K. and Tanaka, O. (1979) *Tetrahedron* **35**, 1427.
17. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The*

Systematic Identification of Flavonoids, p. 261. Springer, Berlin.
18. Guinaudeau, H., Seligmann, O., Wagner, H. and Neszmelyi, A. (1981) *Phytochemistry* **20**, 1113.
19. Harborne, J. B. and Williams, C. A. (1975) in *The Flavonoids, Part I* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds) p. 393. Academic Press, New York.
20. Hirakura, K., Fukai, T., Hano, Y. and Nomura, T. (1985) *Phytochemistry* **24**, 159.
21. Arnone, A., Cardillo, G., Merlini, L. and Mondelli, R. (1967) *Tetrahedron Letters* 4201.
22. Tachibana, K., Scheuer, P. J., Tsukitani, Y., Kikuchi, H., Van Engen, D., Clardy, J., Copichand, Y. and Schmitz, F. J. (1981) *J. Am. Chem. Soc.* **103**, 2469.
23. Wehrli, F. W. (1975) *J. Chem. Soc. Chem. Comm.* 663.
24. Uzawa, J. and Uramoto, M. (1979) *Org. Magn. Res.* **12**, 612.