Gmelinosides A−L, Twelve Acylated Iridoid Glycosides from *Gmelina arborea*

Mohammed Hosny[†] and John P. N. Rosazza*

Division of Medicinal and Natural Products Chemistry and Center for Biocatalysis and Bioprocessing, College of Pharmacy, The University of Iowa, Iowa City, Iowa 52242

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Besides the known iridoids 6-*O*-α-L-rhamnopyranosylcatalpol (**1**), 6-*O*-(3″-*O*-*trans*-feruloyl)-α-L-rhamnopyranosylcatalpol (**14**), 6-*O*-(2″-*O*-acetyl-3″,4″-*O*-di-*trans*-cinnamoyl)-α-L-rhamnopyranosylcatalpol (**15**) and the known phenylpropanoid glycosides verbascoside (acteoside) and martynoside, 12 new acylated iridoid glycosides named gmelinosides A−L (**2**−**13**) have been isolated from the leaves of *Gmelina arborea*. These compounds were structurally characterized using a variety of spectral methods.

Iridoid glycosides occupy an important position in the field of natural product chemistry and biology because they provide a structural link between terpenoids and indole alkaloids and display an interesting spectrum of biological activities.[1] The isolation of monoacyl, diacyl, and triacyl derivatives of 6-*O*-α-L-rhamnopyranosylcatalpol has been reported from several plant families including the Buddlejaceae, Scrophulariaceae, and Verbenaceae.[2−19] The genus *Gmelina* belongs to the subfamily Viticoideae, of the Verbenaceae and is a subcosmopolitan genus centered in the warm temperate regions of the Mediterranean and South Asia. The important commercial timber species, *Gmelina arborea* Roxb., is found in many ornamental gardens in Egypt. This plant has been used in Indian traditional systems of medicine in the form of a decoction as a diuretic, for loosening phlegm, as an appetite stimulant and a galactagogue, and for the treatment of liver disorders.[20−26] Its chemical constituents have been examined, and the isolation of luteolin[27] and indole alkaloids[28] from the leaves has been reported. The occurrence of octacosanol,[29] cluytyl ferulate,[30] and lignans (including arboreol, isoarboreol, methyl arboreol, arborone, gmelanone, gummadiol, gmelanone, and 7-oxodihydrogmelinol[31−34]) in the heartwood has also been noted. A literature survey indicated no previously reported iridoid glycosides in the genus *Gmelina*. Our present research on the leaves of *G.arborea* has resulted in the isolation of several new monoacylated, diacylated, and triacylated iridoid glycosides. We wish to report herein the isolation and structure elucidation of 12 new acylated iridoid glycosides (**2**−**13**) isolated from the leaves of *G. arborea*, in addition to three known iridoid glycosides (**1**, **14**, **15**) and two known phenylpropanoid glycosides.

Results and Discussion

The water-soluble portion of the methanolic extract of *G. arborea* leaves was fractionated by solvent partitioning. A combination of polyamide and Si gel column chromatography followed by further purification using reversed-phase chromatography (RP-18) and Sephadex LH 20 column chromatography led to the isolation of several new acylated gmelinosides glycosides A−L (**2**−**13**) in addition to several known iridoid and phenylpropanoid glycosides. These known compounds were identified by direct comparison with authentic samples and by spectroscopic analysis (UV, IR, ^{1}H and ^{13}C NMR, and FABMS) as 6-*O*-α-L-rhamnopyranosylcatalpol (**1**),[12] 6-*O*-(3″-*O*-*trans*-feruloyl)-α-L-rhamnopyranosylcatalpol (**14**),[15] 6-*O*-(2″-*O*-acetyl-3″, 4″-*O*-di-*trans*-cinnamoyl)-α-L-rhamnopyranosylcatalpol (**15**),[8] verbascoside,[35] and martynoside,[36] respectively. All ^{13}C NMR multiplicities of gmelinosides A−L (**2**−**13**) were confirmed by DEPT measurements, and signal connectivities were determined by HMBC and HMQC. The new iridoid constituents (**2**−**13**) of *G. arborea* contained the same iridoid enol−ether system of 6-*O*-α-L-rhamnopyranosylcatalpol, and were esterified with cinnamoyl or benzoyl derivatives attached to different hydroxyl groups on the sugars or the aglycon moieties. In general, carbons bearing esterifed hydroxyl groups were readily identified by HMBC-connectivity analysis and by the usual downfield shift of the carbon bearing the ester groups relative to the nonesterified equivalent. The 12 new iridoids (**2**−**13**) were identified as follows.

Gmelinoside A (**2**) gave *m*/*z* 639.2293 $[M + H]^+$, for $C_{30}H_{38}O_{15}$ by positive-ion HRFABMS. The ^{1}H (Experimental Setion) and ^{13}C NMR spectra of **2** (Table 1) were similar to those of **1**, except for signals arising from an acyl moiety. The ^{1}H NMR spectrum showed an AB-system (J_{AB} = 16.0 Hz) centered at δ 6.58 and 7.73, indicating the (*E*)-geometry of a *trans*-cinnamoyl double bond. Placement of the acyloxy unit at C-10 in **2** was suggested from the H-10 resonance, which was expected as an AB or AX spin system at δ 5.69 and 4.65. The ^{13}C NMR spectrum of **2** (Table 1), showed the expected downfield shift (δ +4.36) for C-10 and an upfield shift (δ −3.19) for C-8 when compared to 1. The linkage of the ester to C-10 was confirmed by an HMBC cross peak between H-10B and the carbonyl carbon at δ 168.30. The carbonyl carbon was also coupled to the doublets at δ 6.58 (J = 16 Hz) for H-α and δ 7.73 (J = 16 Hz) for H-β. The position of the cinnamoyl moiety was also confirmed by carrying out low-power selective proton ^{13}C NMR decoupling of the methylene proton centered

* To whom correspondence should be addressed. Tel.: (319) 335-4902. Fax: (319) 335-4901. E-mail: john-rosazza@uiowa.edu.
[†] Present address: Al-Azhar University, Faculty of Pharmacy, Department of Pharmacognosy, Cairo, Egypt.

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Table 1. ^{13}C NMR Spectral Data for Compounds **1**−**13**[a] (90 MHz, CD_3OD, TMS as Internal Standard)

carbon	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
aglycon													
1	94.41 d	95.21 d	95.14 d	95.23 d	95.63 d	95.14 d	95.34 d	95.10 d	95.81 d	95.27 d	95.17 d	95.65 d	95.15 d
3	141.69 d	142.40 d	142.52 d	142.24 d	142.35 d	142.65 d	142.98 d	142.16 d	142.40 d	142.08 d	142.50 d	142.30 d	142.10 d
4	103.16 d	103.50 d	103.24 d	103.36 d	103.46 d	103.42 d	103.28 d	103.76 d	103.58 d	103.10 d	103.40 d	103.20 d	103.40 d
5	36.66 d	37.36 d	37.19 d	37.20 d	37.26 d	37.35 d	37.43 d	36.86 d	37.06 d	37.65 d	37.30 d	37.45 d	37.24 d
6	83.37 d	84.18 d	84.16 d	84.12 d	84.36 d	84.55 d	84.19 d	84.23 d	84.08 d	84.72 d	84.57 d	83.43 d	84.05 d
7	58.63 d	59.48 d	59.36 d	59.58 d	59.60 d	59.10 d	59.32 d	59.14 d	58.42 d	59.38 d	59.66 d	58.98 d	59.26 d
8	66.38 s	63.19 s	63.06 s	63.08 s	63.25 s	63.10 s	63.27 s	66.08 s	65.89 s	66.14 s	66.58 s	66.20 d	66.56 d
9	42.74 d	43.34 d	43.62 d	43.60 d	43.48 d	43.32 d	43.46 d	43.74 d	43.24 d	43.58 d	43.34 d	42.86 d	43.27 d
10	60.51 t	64.87 t	64.08 t	64.14 t	64.05 t	64.88 t	64.72 t	61.56 t	62.07 t	61.12 t	61.17 t	61.58 t	61.38 t
glucose													
1′	100.30 d	100.52 d	99.73 d	101.00 d	101.28 d	100.14 d	102.44 d	101.81 d	100.12 d	102.20 d	99.70 d	99.77 d	100.30 d
2′	74.30 d	75.54 d	74.85 d	74.38 d	74.64 d	74.42 d	73.49 d	73.90 d	74.14 d	74.92 d	74.83 d	73.31 d	74.81 d
3′	77.52 d	77.69 d	77.67 d	78.13 d	78.85 d	78.36 d	77.19 d	78.62 d	77.79 d	77.49 d	77.68 d	77.24 d	78.62 d
4′	71.28 d	71.86 d	71.81 d	71.90 d	71.35 d	71.05 d	71.61 d	71.48 d	71.50 d	71.00 d	71.78 d	71.31 d	71.77 d
5′	77.85 d	78.06 d	77.75 d	78.39 d	78.08 d	78.12 d	74.40 d	77.81 d	78.00 d	78.63 d	78.64 d	77.37 d	77.66 d
6′	61.20 t	61.73 t	62.42 t	62.88 t	62.46 t	62.06 t	63.68 t	62.73 t	62.92 t	62.40 t	62.96 t	61.25 t	61.94 t
rhamnose													
1″	99.21 d	99.84 d	97.86 d	99.97 d	99.88 d	98.91 d	100.69 d	98.30 d	97.74 d	98.17 d	98.91 d	98.85 d	99.69 d
2″	72.47 d	72.34 d	72.28 d	72.79 d	72.68 d	73.86 d	70.54 d	71.59 d	71.76 d	73.74 d	73.92 d	70.14 d	70.06 d
3″	72.23 d	72.18 d	72.16 d	72.33 d	71.34 d	70.10 d	71.11 d	71.18 d	70.88 d	69.76 d	70.17 d	73.29 d	73.21 d
4″	73.74 d	73.59 d	72.81 d	73.08 d	73.47 d	74.95 d	71.87 d	72.09 d	72.89 d	74.11 d	74.62 d	72.38 d	72.53 d
5″	69.85 d	69.28 d	68.95 d	69.01 d	69.64 d	68.70 d	68.53 d	69.65 d	68.78 d	68.57 d	68.35 d	67.95 d	68.27 d
6″	18.44 d	18.28 q	17.81 q	18.33 q	18.06 q	17.85 q	18.55 q	17.78 q	18.41 q	17.20 q	18.07 q	17.33 q	17.84 q
ester[b]	**A**	**A**	**B**	**C**	**D**	**E**	**D**	**D**	**B**	**F**	**F**	**A**	
1‴	135.80 s	135.50 s	127.17 s	126.88 s	127.38 s	124.12 s	127.34 s	129.89 s	127.57 s	131.20 s	129.90 s	135.36 s	
2‴	130.10 d	129.78 d	130.72 d	114.59 d	111.77 d	130.28 d	112.15 d	111.86 d	131.68 d	130.80 d	129.20 d	130.10 d	
3‴	129.33 d	129.50 d	116.37 d	149.58 s	149.76 s	116.10 d	151.93 s	150.48 s	116.87 d	129.60 d	128.80 d	129.40 d	
4‴	131.63 d	131.95 d	161.37 s	146.32 s	150.21 s	163.56 s	149.22 s	150.24 s	161.56 s	134.40 d	133.50 d	131.80 d	
5‴	129.33 d	129.50 d	116.37 d	116.20 d	116.56 d	116.10 d	116.94 d	116.45 d	116.87 d	129.60 d	128.80 d	129.40 d	
6‴	130.10 d	129.78 d	130.72 d	123.58 d	124.33 d	130.28 d	123.72 d	124.30 d	131.68 d	130.80 d	129.20 d	130.10 d	
α	118.90 d	117.93 d	114.64 d	115.70 d	115.06 d		115.78 d	115.66 d	114.72 d			118.10 d	
β	146.70 d	147.60 d	147.34 d	147.76 d	147.46 d		148.14 d	147.90 d	147.38 d			147.30 d	
C═O	168.30 s	167.50 s	169.10 s	168.20 s	168.76 s	168.90 s	168.40 s	168.00 s	168.35 s	167.70 s	167.20 s	167.60 s	
1⁗							128.00 s	129.21 s	126.90 s	131.10 s	129.10 s		
2⁗							111.95 d	111.07 d	131.30 d	130.60 d	129.20 d		
3⁗							150.63 s	149.53 s	115.35 d	129.40 d	128.50 d		
4⁗							148.86 s	149.97 s	159.62 s	134.40 d	133.40 d		
5⁗							114.90 d	116.34 d	115.35 d	129.40 d	128.50 d		
6⁗							123.38 d	124.00 d	131.30 d	131.10 d	129.10 d		
α							115.49 d	115.20 d	114.46 d				
β							147.60 d	147.38 d	147.10 d				
C═O							167.92 s	166.59 s	167.78 s	167.30 s	165.10 s		
OCH_3					56.54 q		56.48 q	56.82 q					
							56.35 q	56.05 q					
COCH_3		171.70 s			171.26 s	171.42 s		171.22 s				171.29 s	
		171.87 s			171.89 s								
C O*C*H_3		20.73 q			20.45 q	20.90 q		20.72 q				20.62 q	
		20.65 q			20.20 q								

[a] Assignments were confirmed by HMBC and HMQC spectra at 600 MHz. [b] A = cinnamoyl, B = coumaroyl, C = caffeoyl, D = feruloyl, E = *p*-OH-benzoyl, F = benzoyl.

at δ 5.69 (H-10B), where in signals for C-10 (δ 64.87), the cinnamoyl carbonyl (δ 168.30) and C-8 (δ 63.19) collapsed. This significant coupling pattern and the experimental data obtained were also in good agreement with the reported data for globularin with a similar acyl moiety attached to the iridoid skeleton.[18−21] Confirmation of the sugar sequence in 2 resulted from 2D $^1H-^1H$ NOESY measurements. Thus, the anomeric proton of the *β*-D-glucosyl moiety (δ 4.78, d, J = 7.9 Hz) showed an NOE to H-1 (δ 5.01) as well as to the anomeric proton of the α-L-rhamnose moiety (δ 5.10, d, J = 1.7 Hz) to H-6 (δ 4.04). Heptaacetylgmelinoside A (**2a**) ($C_{44}H_{52}O_{22}$) gave fragment ions at m/z 624 $[(M + Na) - 331]^+$ for loss of a [2,3,4,6-*O*-tetraacetylglucose-oxonium]$^+$ ion and m/z 682 $[(M + Na) - 273]^+$ for the loss of a [2,3,4-*O*-triacetylrhamnose-oxonium]$^+$ ion. The ^1H NMR spectrum of **2a** revealed seven acetyl signals, thus confirming the presence of unsubstituted glucosyl and rhamnosyl moieties in **2**. In **2a,** no downfield shifts for the H-10 signals of the aglycon moiety (δ 4.66, H-10A) and (δ 5.62, H-10B) occurred, supporting C-10 as the site of cinnamoyl acylation. The 2D $^1H-^1H$ COSY and $^1H-^{13}C$ HMBC and HMQC NMR spectra of **2a** confirmed the structure of **2** as 10-*O*-*trans*-cinnamoyl-6-*O*-α−L-rhamnopyranosylcatalpol, for which we propose the trivial name gmelinoside A.

Gmelinoside B (**3**), $C_{34}H_{42}O_{17}$, gave an FABMS fragment at m/z 231, suggesting a [diacetylrhamnose-oxonium]$^+$ ion. The ^1H and ^{13}C NMR data for **3** indicated a structure like **2**, with characteristic signals for cinnamic acid and 6-*O*-α-L-rhamnopyranosylcatalpol moieties and two acetyl groups. The $^1H-^1H$ COSY spectrum correlated the anomeric rhamnose proton (δ 5.12, d, J = 1.7 Hz, α-glycoside) with H-2″ (δ 5.31) (axial−equatorial coupling), which, in turn, was coupled to the doublet of doublets at δ 5.37 (H-3″) (axial−axial

coupling), indicating the substitution of acetyl moieties at C-2″ and C-3″. HMQC established connectivities between C-2″ (δ 72.28) and H-2″ (δ 5.31), and C-3″ (δ 72.16) and H-3″ (δ 5.37). In the HMBC spectrum, signals for H-10B, H-2″, and H-3″ of **3** were long-range coupled to the carbon signals at δ 167.50 (carbonyl carbon of an *E*-cinnamoyl moiety), and δ 171.87 and 171.70 (acetyl carbonyls), respectively. The structure of **3** was thus assigned as 10-*O*-*trans*-cinnamoyl-6-*O*-(2″,3″-di-*O*-acetyl)-α-L-rhamnopyranosylcatalpol, and this isolate was named gmelinoside B.

Gmelinoside C (**4**), $C_{30}H_{38}O_{16}$, gave ^{1}H and ^{13}C NMR spectra similar to those of **2** except for signals arising from the ester moiety. Hydrolysis of **4** gave (*E*)-*p*-coumaric acid and 6-*O*-α-L-rhamnopyranosylcatalpol by TLC. The ^{13}C NMR spectrum showed resonances for a *(E)*-*p*-coumaroyl unit (Table 1). Attachment of the (*E*)-*p*-coumaroyl unit at C-10 was confirmed by HMBC by a correlation between H-10B (δ 5.65, d, J = 13.0 Hz) and the coumaroyl carbonyl carbon (δ 169.10). Selective decoupling of the H-10 proton at δ 5.65 caused the signals for C-10 (δ 64.14), C═O (δ 169.10), and C-8 (δ 63.08) to collapse, confirming the position of the ester at C-10. Thus, **4** was assigned 10-*O*-*trans*-*p*-coumaroyl-6-*O*-α-L-rhamnopyranosylcatalpol, and named gmelinoside C.

Gmelinoside D (**5**), $C_{30}H_{38}O_{17}$, contained a *trans*-caffeoyl ester moiety by ^{1}H NMR, confirmed by a *m/z* 163 peak in the MS. Hydrolysis of **5** yielded **1** and caffeic acid by TLC. The ^{13}C NMR and DEPT spectra of this ester moiety (Table 1) were in full agreement with those of other caffeoyl esters.[22] Following the same procedures used in identifying **2**−**4**, the H-10A (δ 4.68, d, J = 13.0 Hz) and H-10B (δ 5.86, d, J = 13.0 Hz) signals from the 6-*O*-α-L-rhamnopyranosylcatalpol were shifted downfield versus analogous data for **1**, indicating C-10 to be the site of acylation. Such spectral evidence pointed to structure **5** for gmelinoside D (10-*O*-*trans*-caffeoyl-6-*O*-α-L-rhamnopyranosylcatalpol).

Gmelinoside E (**6**), $C_{35}H_{44}O_{19}$, gave HRFABMS fragment ions at *m/z* 177 (loss of a feruloyl residue), and *m/z* 231 (loss of a diacetylrhamnose-oxonium)$^+$ ion. The ^{1}H and ^{13}C NMR spectra of **6** exhibited characteristic signals for an (*E*)-ferulic acid moiety. Relative to **1**, shifts of the signals for C-10 (+δ 4.37) and C-8 (−δ 3.28) (Table 1) precluded a feruloyl moiety attachment at the latter position. An HMBC correlation between H-10 and the carbonyl carbon of the *trans*-feruloyl moiety suggested the location of the feruloyl ester at the C-10 hydroxyl group. The ^{1}H NMR spectral data of the rhamnosyl moiety of **6** were similar to those of **3**, with one acetyl group at C-2″. The triplet signal for H-4″ (δ 4.92, J = 9.6 Hz) placed the other acetyl group on a carbon bearing a proton with a diaxial relationship. From the ^{13}C NMR spectrum of **6** (Table 1) the shielding effect (−δ 3.13 ppm) for C-3″ versus **1** was ascribed to the cumulative β-effects of acetyl groups on C-2″ and C-4″. Connectivities between C-2″ (δ 73.86) and H-2″ (δ 5.43), and C-4″ (δ 74.95) and H-4″ (δ 4.92), by HMQC, and long-range connectivities (^3J) between *CO*CH$_3$ (δ 171.26) and H-2″, *CO*CH$_3$ (δ 171.89) and (H-4″) and C-α (δ 115.06) and H-10 in the HMBC spectrum, showed C-2″, C-4″, and C-10 to be the sites of acylation. The ^{1}H NMR spectrum of the hexaacetate (**6a**) gave six acetate signals belonging to one phenolic group and five alcoholic acetate groups. No downfield shift was observed for the signals for H-10, H-2″, and H-4″, confirming these to be the sites of acylation. The FABMS of **6a** for $C_{47}H_{56}O_{25}$ also gave a significant fragmention at *m/z* 219 [4-*O*-acetyl feruloyl]$^+$ and characteristic ions at *m/z* 331 for the loss of a [2,3,4,6-*O*-tetraacetylglucose-oxonium]$^+$ ion and *m/z* 273 for the loss of a [2,3,4-*O*-triacetylrhamnose-oxonium]$^+$ ion. Thus, the structure of **6** is 10-*O*-*trans*-feruloyl-6-*O*-(2″,4″-di-*O*-acetyl)-α-L-rhamnopyranosylcatalpol, and it was named gmelinoside E.

Gmelinoside F (**7**), $C_{30}H_{38}O_{17}$, showed FABMS ions at *m/z* 138 and 121, and its ^{1}H NMR spectrum suggested the presence of a *p*-hydroxybenzoyl moiety (AA′BB′ system). Hydrolysis of **7** gave **1** and *p*-hydroxybenzoic acid by TLC. HMQC and HMBC spectra and selective INEPT NMR clearly indicated the location of the acyl unit at C-10 of 6-*O*-α-L-rhamnopyranosylcatalpol. Six signals could be assigned to a β-glucopyranosyl moiety acetylated at C-6′ as seen by a downfield shift for C-6′ and an upfield shift for C-5′ in **7** versus **1**−**6** (Table 1). An HMBC cross peak between H-6′ and the acetyl carbonyl signal at δ 171.42 was observed. Thus, the structure of gmelinoside F (**7**) was assigned as 10-*O*-*p*-hydroxbenzoyl-6-*O*-(6′-*O*-acetyl)-α-L-rhamnopyranosylcatalpol.

The HRFABMS of gmelinoside G (**8**) gave $C_{41}H_{48}O_{20}$, and the ^{1}H NMR spectrum contained sets of signals for two feruloyl moieties. The FABMS demonstrated a characteristic fragment at *m/z* 500, arising from a [diferuloylrhamnose-oxonium]$^+$ ion. Hydrolysis followed by TLC indicated that **8** contained 6-*O*-α-L-rhamnopyranosylcatalpol and ferulic acid. The ^{13}C NMR and DEPT spectra of **8** confirmed the presence of two *trans*-disubstituted double bonds, two trisubstituted benzene rings, two methoxyl groups, and two ester carbonyls, as well as the carbon atoms belonging to 6-*O*-α-L-rhamnopyranosylcatalpol (Table 1). Differences in ^{13}C NMR chemical shifts between **8** and **1** for C-1″ (−δ 0.91), C-2″ (−δ 0.88), C-3″ (−δ 1.05), and C-4″ (−δ 1.65) (β-effect due to acylation) suggested that the two feruloyl groups were attached to C-2″ and C-3″ of the rhamnose moiety. This was confirmed by the homonuclear ^{1}H−^{1}H correlation COSY NMR spectrum of **8**. The anomeric proton (1″) of rhamnose (δ 5.10) was correlated only with the H-2″ signal (δ 5.33), which in turn, was coupled to the H-3″ signal (δ 4.98), confirming the acylated positions to be C-2″ and C-3″. HMBC confirmed the attachments of two feruloyl moieties at C-2″ and C-3″ of rhamnose. A ^3J (COCH) coupling between the carbonyl carbon signals and H-2″ and H-3″ of α-rhamnose placed the two feruloyl moieties at these positions. The ^{1}H-NMR spectrum of the octaacetate derivative **8a** showed two acetyl signals for phenolic hydroxyl groups and six aliphatic hydroxyl groups. The significant downfield shift of the methine proton of position C-4″ in **8a** clearly showed that the nonesterified hydroxyl group of **8** was at C-4″ and that the feruloyl groups were esterified at C-2″ and C-3″. Thus, the structure of gmelinoside G (**8**) was assigned as 6-*O*- (2″,3″-*O*-di-*trans*-feruloyl)-α-L-rhamnopyranosylcatalpol.

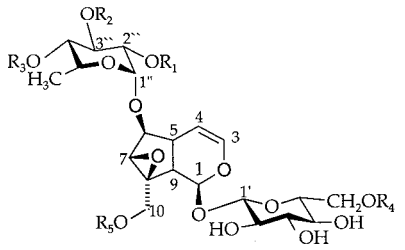
The HRFABMS of gmelinoside H (**9**) ($C_{43}H_{50}O_{21}$) and its ^{1}H NMR, ^{13}C NMR, and DEPT spectra suggested

that this compound had two feruloyl esters and one acetyl ester. As with **8**, the HMBC spectrum of **9** confirmed the attachment of feruloyl moieties at C-2″ and C-3″. The H-4″ signal (δ 4.98, J = 9.9 Hz) was deshielded by the geminal acetoxyl group. HMBC correlations were clear between the methyl proton (δ 1.96) of the acetyl group and H-4″ (δ 4.98) and the acetyl carbonyl carbon (δ 171.22), indicating acylation at this location. The HRFABMS of **9** also gave an *m*/*z* 541 fragment ion (rhamnose moiety esterified with two feruloyl units and one acetyl ester unit). Acetylation of **9** gave a heptaacetate (**9a**), whose ^{1}H NMR and TLC data agreed with those of the octaacetate of **8a** (see Experimental Section). Thus, **9** was established as 6-*O*-(4″-*O*-acetyl-2″,3″-*O*-di-*trans*-feruloyl)-α-L-rhamnopyranosylcatalpol.

Gmelinoside I (**10**), gave $C_{39}H_{44}O_{18}$ by HRFABMS. In its 1D and 2D ^{1}H−^{1}H homonuclear COSY and NOESY NMR spectra, signals for two *p*-OH-cinnamic acid moieties were observed. The two aromatic residues were clearly indicated by the negative-ion FABMS of **10**, due to successive elimination of two *p*-coumaroyl groups and one rhamnose unit. Hydrolysis of **10** produced *p*-coumaric acid along with 6-*O*-α-L-rhamnopyranosylcatalpol, as determined by TLC. In the manner discussed earlier, the COSY, HMQC, and HMBC spectra of **10** enabled assignment of the two *p*-coumaroyl esters at positions C-2″ and C-4″ on the rhamnose moiety. Thus, the structure of compound **10** was assigned as 6-*O*-(2″,4″-*O*-di-trans-*p*-coumaroyl)-α-L-rhamnopyranosylcatalpol (gmelinoside I).

Gmelinosides J (**11**) and K (**12**) each gave $C_{35}H_{40}O_{16}$ by HRFABMS. The ^{1}H NMR spectrum of each compound contained signals for two benzoyl units. The decoupled ^{13}C NMR spectra of **11** and **12** showed 35 carbons, the multiplicities of which were established by DEPT (Table 1). Each compound showed a fragment ion at *m*/*z* 355 (rhamnose moiety esterified with two benzoic acid substituents) in its HRFABMS. ^{1}H and ^{13}C NMR spectral analysis (COSY, HMQC, HMBC, and NOE) showed the acylated positions to be C-2 and C-4 of rhamnose in **11** and C-3 and C-4 of rhamnose in **12**. Thus, **11** (gmelinoside J) was assigned as 6-*O*-(2″,4″-*O*-di-benzoyl)-α-L-rhamnopyranosylcatalpol and **12** (gmelinoside K) as 6-*O*-(3″,4″-*O*-di-benzoyl)-α-L-rhamnopyranosylcatalpol.

By HRFABMS gmelinoside L (**13**) was assigned as $C_{32}H_{40}O_{16}$, and gave a strong fragment ion at *m*/*z* 319 by elimination of a rhamnosyl moiety esterified with cinnamic and acetic acid units. Hydrolysis followed by TLC indicated that **13** contained 6-*O*-α-L-rhamnopyranosylcatalpol and cinnamic acid. ^{1}H−^{1}H COSY, ^{1}H−^{13}C HMBC, and HMQC data (Table 1) confirmed that both a *trans*-cinnamoyl moiety and an acetyl group were present in **13**. The relatively lowfield positions of the methine protons at C-3″ and C-4″ showed that the oxygen atoms at these positions were acylated. HMBC clearly indicated that H-3″ and H-4″ were long-range coupled to *CO*CH$_3$ (δ 171.29) and the *trans*-cinnamoyl to C=O (δ 167.60), respectively. The structure of gmelinoside L (**13**) was therefore established as 6-*O*-(3″-*O*-acetyl-4″-*O*-*trans*-cinnamoyl)-α-L-rhamnopyranosylcatalpol.



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2	H	H	H	H	A
3	Ac	Ac	H	H	A
4	H	H	H	H	B
5	H	H	H	H	C
6	Ac	H	Ac	H	D
7	H	H	H	Ac	E
8	D	D	H	H	H
9	D	D	Ac	H	H
10	B	H	B	H	H
11	F	H	F	H	H
12	H	F	F	H	H
13	H	Ac	A	H	H
14	H	D	H	H	H
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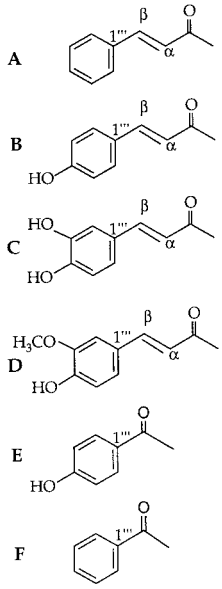

Experimental Section

General Experimental Procedures. Flash column liquid chromatography, was performed using J. T. Baker glassware with 40-μm Si gel (Baker) and Sepralyte C_{18} (40 μm) as the adsorbents. TLC was carried out on precoated Si gel 60 F_{254} (Merck) plates. Developed chromatograms were detected by spraying with 1% vanillin−H_2SO_4, followed by heating at 100 °C for 5 min. UV spectra were run on a Hitachi 340 spectrophotometer. IR spectra were obtained using a Nicolet 205 FT-IR spectrometer connected to a Hewlett−Packard ColorPro plotter. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker NM-360 spectrometer operating at 360 MHz and 90 MHz, respectively. All spectra were obtained in CD_3OD or $CDCl_3$ using TMS as internal standard, with the chemical shifts expressed in δ and the coupling constants (J) in Hz. COSY, NOESY, HMBC, and HMQC NMR experiments were carried out using a Bruker AMX-600 highfield spectrometer equipped with an IBM Aspect-2000 processor and with software VNMR version 4.1, using TMS as an internal standard in appropriate solvents. FABMS spectra were performed using a VG-ZAB-HF reversed geometry (BE configuration, where B is a magnetic sector and E is an electrostatic analyzer) mass spectrometer.

Plant Material. The leaves of *Gmelina arborea* Roxb. were collected in January 1995, from Al-Orman Garden, Giza, Egypt. The plant was kindly authenticated by Prof. Dr. M. N. El-Hadidy, Faculty of Science, Cairo University. A voucher specimen is deposited in the Pharmacognosy Department, Faculty of Pharmacy, Al-Azhar University, Cairo, Egypt.

Extraction and Isolation. Powdered air-dried leaves (800 g) were exhaustively extracted at room tempera-

ture with MeOH (3 × 5 L). The combined MeOH extracts were concentrated in vacuo at 40 °C to a brown residue (157 g). The concentrated extract was suspended in H_2O (100 mL) and filtered through Celite. The filtrate and washings were combined and defatted with petroleum ether. The concentrated defatted crude extract (78 g) was partitioned with $CHCl_3$ and *n*-BuOH. The *n*-BuOH-soluble fractions were pooled and concentrated in vacuo at 40 °C to afford a residue (37 g). An aliquot of the extract (30 g) was chromatographed on a polyamide column (3.5 × 90 cm), eluting with H_2O followed by increasing concentrations of MeOH to yield six main fractions (A−F): A (11.5 g), B (3.2 g), C (4.65 g), D (1.35 g), E (2.2 g), and F (653 mg). Fraction A (11.5 g), which was rich in iridoids, was subjected to column chromatography over Si gel (3.5 × 90 cm) using $CHCl_3$−MeOH−H_2O (80:20:1→ 60:40:4) to yield seven main fractions. Fraction A_1 (1.85 g) was applied to a flash column (2 × 50 cm, stationary phase: Sepralyte C_{18} 40 μm using H_2O−MeOH gradient solvent system (10→ 45%) at a flow rate 2 mL/min to yield compound **1** (39 mg) and a mixture of **2** and **3** (757 mg). The mixture of **2** and **3** was then separated on a Si gel flash column eluted with $CHCl_3$−MeOH−H_2O (80:20:2→ 70:30:3) to afford compounds **2** (308 mg) and **3** (159 mg), respectively. Final purification of compounds **2** and **3** over a Sephadex LH-20 column (1.5 × 60 cm) eluted with MeOH yielded **2** (283 mg) and **3** (139 mg), respectively.

Fractions A_2 (3.92 g), A_3 (2.34 g), A_4 (1.56 g), A_5 (523 mg), A_6 (370 mg), and A_7 (235 mg) were separately subjected successively to column chromatography on polyamide, [eluting with mixtures of H_2O−MeOH (9:1→ 7:3)], normal-phase Si gel [40 μm, using $CHCl_3$−MeOH−H_2O (90:10:1→ 60:40:4), EtOAc−MeOH−H_2O (40:2:1→ 30:2:1), EtOAc−MeOH−H_2O (100:16.5:13.5)], Sepralyte C_{18} [40 μm, using an H_2O−MeOH gradient solvent system (10→ 45%) at a flow rate 2 mL/min], and finally Sephadex LH-20 (eluted with MeOH), to afford compounds **4** (203 mg) **5** (116 mg), **6** (76 mg), **7** (50 mg), **8** (66 mg), **9** (71 mg), **10** (27 mg), **11** (16 mg), **12** (11 mg), **13** (59 mg), **14** (15 mg), and **15** (12 mg), respectively. Fraction C (4.65 g) was further purified by flash column chromatography (3.5 × 90 cm) over Si gel using EtOAc−MeOH−H_2O (100:16.5:13.5) to give two fractions C_1 (1.97 g) and C_2 (215 mg). Fraction C_1 was rechromatographed further by flash column chromatography over Sepralyte C_{18} (H_2O−MeOH, 20→35%), to yield compounds **16** (verbascoside, 775 mg) and **17** (martynoside, 98 mg).

6-*O*-α-L-Rhamnopyranosylcatalpol (1): obtained as a white amorphous powder (39 mg); $[\alpha]^{25}_D$ −126.5° (*c* 0.50, MeOH); UV (MeOH) λ_{max} (log ϵ) 208 (4.10) nm; IR (KBr) ν_{max} 3450 (OH), 1635 (C=C) cm^{-1}; ^1H NMR (CD_3OD, 360 MHz) aglycon moiety δ 5.05 (1H, d, J = 9.2 Hz, H-1), 6.38 (1H, dd, J = 6.0, 1.8 Hz, H-3), 5.10 (1H, dd, J = 6.0, 4.3 Hz, H-4), 2.49 (1H, m, H-5), 4.03 (1H, dd, J = 8.2, 1.8 Hz, H-6), 3.70 (1H, s, H-7), 2.66 (1H, dd, J = 9.6, 7.7 Hz, H-9), 3.83 (1H, d, J = 13.0 Hz, H-10A), 4.18 (1H, d, J = 13.0 Hz, H-10B); glucosyl moiety δ 4.80 (1H, d, J = 8.0 Hz, H-1′), 3.17 (1H, dd, J = 7.9, 9.1 Hz, H-2′), 3.36 (1H, t, J = 9.1 Hz, H-3′), 3.23 (1H, t, J = 9.1 Hz, H-4′), 3.33 (1H, m, H-5′), 3.65 (1H, dd, J = 12.0, 6.7 Hz, H-6′A), 3.94 (1H, dd, J = 12.0, 2.0 Hz, H-6′B); rhamnosyl moiety δ 5.10 (1H, d, J = 1.6 Hz, H-1″), 3.93 (1H, dd, J = 3.3, 1.5 Hz, H-2″), 3.67 (1H, dd, J = 3.3, 9.5 Hz, H-3″), 3.65 (1H, t, J = 9.5 Hz, H-4″), 3.81 (1H, dd, J = 10.2, 6.0 Hz, H-5″), 1.26 (3H, d, J = 6.3 Hz, H-6″); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); FABMS *m/z* 531 $[M + Na]^+$, 509 $[M + H]^+$. Positive identification was achieved by comparison with literature data.[12]

Gmelinoside A (2): obtained as a white amorphous powder (283 mg); $[\alpha]^{25}_D$ −98.8° (*c* 0.72, MeOH); UV (MeOH) λ_{max} (log ϵ) 222 (4.18), 312 (4.32) nm; IR (KBr) ν_{max} 3400 (OH), 1720 (C=O), 1630 (C=C), 1655 (C=C iridoid), 1540 (aromatic) cm^{-1}; ^1H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.01 (1H, d, J = 9.6 Hz, H-1), 6.38 (1H, dd, J = 6.5, 1.7 Hz, H-3), 5.06 (1H, dd, J = 6.5, 4.5 Hz, H-4), 2.45 (1H, m, H-5), 4.04 (1H, dd, J = 8.2, 1.7 Hz, H-6), 3.66 (1H, s, H-7), 2.57 (1H, dd, J = 9.6, 7.6 Hz, H-9), 4.65 (1H, d, J = 13.1 Hz, H-10A), 5.69 (1H, d, J = 13.1 Hz, H-10B); glucosyl moiety δ 4.78 (1H, d, J = 7.9 Hz, H-1′), 3.26 (1H, dd, J = 7.9, 9.2 Hz, H-2′), 3.40 (1H, t, J = 9.2 Hz, H-3′), 3.27 (t, J = 9.2 Hz, H-4′), 3.30 (1H, m, H-5′), 3.63 (1H, dd, J = 11.9, 6.6 Hz, H-6′A), 3.91 (1H, dd, J = 12.0, 2.0 Hz, H-6′B); rhamnosyl moiety δ 5.10 (1H, d, J = 1.7 Hz, H-1″), 3.89 (1H, dd, J = 3.7, 2.0 Hz, H-2″), 3.81 (1H, dd, J = 3.7, 9.3 Hz, H-3″), 3.49 (1H, t, J = 9.5 Hz, H-4″), 3.97 (1H, dd, J = 10.0, 6.2 Hz, H-5″), 1.18 (3H, d, J = 6.3 Hz, H-6″); cinnamoyl moiety δ 7.62 (2H, d, J = 8.0 Hz, H-2‴, 6‴), 6.93 (2H, t, J = 8.0 Hz, H-3‴, 5‴), 7.40 (1H, m, H-4‴), 6.58 (1H, d, J = 16.0 Hz, H-α), 7.73 (1H, d, J = 16.0 Hz, H-β); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS *m/z* 639.2293 $[M + H]^+$, 661 $[M + Na]^+$, (calcd for $C_{30}H_{39}O_{15}$, 639.2289).

Gmelinoside B (3): obtained as an amorphous powder (139 mg); $[\alpha]^{25}_D$ −138.6° (*c* 0.65, MeOH); UV (MeOH) λ_{max} (log ϵ) 218 (4.31), 300 (4.27), 315 (4.30) nm; IR (KBr) ν_{max} 3425 (OH), 1725 (C=O), 1620 (C=C), 1665 (C=C iridoid), 1520 (aromatic) cm^{-1}; ^1H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.08 (1H, d, J = 9.6 Hz, H-1), 6.36 (1H, dd, J = 6.0, 1.7 Hz, H-3), 5.05 (1H, dd, J = 6.0, 5.0 Hz, H-4), 2.53 (1H, m, H-5), 4.07 (1H, dd, J = 8.0, 1.0 Hz, H-6), 3.67 (1H, s, H-7), 2.60 (1H, dd, J = 9.6, 7.7 Hz, H-9), 4.76 (1H, d, J = 12.5 Hz, H-10A), 5.72 (1H, d, J = 12.5 Hz, H-10B); glucosyl moiety δ 4.76 (1H, d, J = 7.9 Hz, H-1′), 3.27 (1H, dd, J = 7.9, 9.3 Hz, H-2′), 3.40 (1H, t, J = 9.1 Hz, H-3′), 3.25 (1H, t, J = 9.1 Hz, H-4′), 3.34 (1H, m, H-5′), 3.67 (1H, dd, J = 11.9, 6.7 Hz, H-6′A), 3.94 (1H, dd, J = 11.9, 2.1 Hz, H-6′B); rhamnosyl moiety δ 5.12 (1H, d, J = 1.7 Hz, H-1″), 5.31 (1H, dd, J = 3.4, 1.7 Hz, H-2″), 5.37 (1H, dd, J = 3.4, 9.9 Hz, H-3″), 3.41 (1H, t, J = 9.9 Hz, H-4″), 3.95 (1H, dd, J = 10.0, 6.0 Hz, H-5″), 1.22 (3H, d, J = 6.2 Hz, H-6″); cinnamoyl moiety δ 7.42 (2H, d, J = 8.2 Hz, H-2‴, H-6‴), 6.79 (2H, t, J = 8.5 Hz, H-3‴, 5‴), 7.43 (1H, m, H-4‴), 6.52 (1H, d, J = 16.0 Hz, H-α), 7.77 (1H, d, J = 16.0 Hz, H-β). 1.89, 2.12 (each 3H, s, OAc); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS *m/z* 723.2507 $[M + H]^+$, 745 $[M + Na]^+$, 231 [diacetylrhamnose-oxonium]$^+$ ion (calcd for $C_{34}H_{43}O_{17}$, 723.2500).

Gmelinoside C (4): obtained as a white amorphous powder (203 mg); $[\alpha]^{25}_D$ −187.3° (*c* 0.82, MeOH); UV (MeOH) λ_{max} (log ϵ) 231 (4.03), 304 (4.13), 338 (4.39) nm; IR (KBr) ν_{max} 3385 (OH), 1695 (C=O), 1610 (C=C), 1650 (C=C iridoid), 1515 (aromatic) cm^{-1}; ^1H NMR (CD_3OD,

600 MHz) aglycon moiety δ 5.13 (1H, d, J = 9.5 Hz, H-1), 6.34 (1H, dd, J = 6.0, 1.8 Hz, H-3), 5.07 (1H, dd, J = 6.0, 4.5 Hz, H-4), 2.55 (1H, m, H-5), 4.04 (1H, dd, J = 8.2, 1.7 Hz, H-6), 3.63 (1H, s, H-7), 2.63 (1H, dd, J = 9.5, 8.0 Hz, H-9), 4.71 (1H, d, J = 13.0 Hz, H-10A), 5.65 (1H, d, J = 13.0 Hz, H-10B); glucosyl moiety δ 4.83 (1H, d, J = 7.8 Hz, H-1′), 3.34 (1H, dd, J = 7.8, 9.5 Hz, H-2′), 3.67 (1H, t, J = 9.5 Hz, H-3′), 3.44 (1H, t, J = 9.5 Hz, H-4′), 3.18 (1H, m, H-5′), 3.54 (1H, dd, J = 12.0, 5.8 Hz, H-6′A), 3.95 (1H, dd, J = 12.0, 1.8 Hz, H-6′B); rhamnosyl moiety δ 5.11 (1H, d, J = 1.8 Hz, H-1″), 3.94 (1H, brd, J = 3.8 Hz, H-2″), 3.90 (1H, dd, J = 3.7, 9.0 Hz, H-3″), 3.68 (1H, t, J = 9.2 Hz, H-4″), 3.88 (1H, dd, J = 10.0, 6.3 Hz, H-5″), 1.29 (3H, d, J = 6.5 Hz, H-6″); coumaroyl moiety δ 7.46 (2H, d, J = 8.7 Hz, H-2‴, 6‴), 6.81 (2H, d, J = 8.7 Hz, H-3‴, 5‴), 6.29 (1H, d, J = 16.1 Hz, H-α), 7.59 (1H, d, J = 16.1 Hz, H-β); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS m/z 655.2243 $[M + H]^+$, 677 $[M + Na]^+$, (calcd for $C_{30}H_{39}O_{16}$, 655.2237).

Gmelinoside D (5): obtained as an amorphous powder (116 mg); $[\alpha]^{25}_D$ −158.5° (c 0.54, MeOH); UV (MeOH) λ_{max} (log ϵ) 223 (4.10), 248 (3.98), 304 (sh 4.17), 332 (4.28), nm; IR (KBr) ν_{max} 3415 (OH), 1686 (C═O), 1623 (C═C), 1660 (C═C iridoid), 1528 (aromatic) cm^{-1}; ^{1}H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.10 (1H, d, J = 9.5 Hz, H-1), 6.43 (1H, dd, J = 6.2, 1.8 Hz, H-3), 5.12 (1H, dd, J = 6.2, 4.4 Hz, H-4), 2.67 (1H, m, H-5), 4.01 (1H, dd, J = 8.0, 1.6 Hz, H-6), 3.63 (1H, s, H-7), 2.59 (1H, dd, J = 9.5, 8.2 Hz, H-9), 4.68 (1H, d, J = 13.0 Hz, H-10A), 5.86 (1H, d, J = 13.0 Hz, H-10B); glucosyl moiety δ 4.98 (1H, d, J = 8.0 Hz, H-1′), 3.43 (1H, dd, J = 8.0, 9.1 Hz, H-2′), 3.49 (1H, t, J = 9.1 Hz, H-3′), 3.38 (1H, t, J = 9.0 Hz, H-4′), 3.12 (1H, m, H-5′), 3.65 (1H, dd, J = 11.7, 5.7 Hz, H-6′A), 3.88 (1H, dd, J = 11.7, 1.8 Hz, H-6′B); rhamnosyl moiety δ 5.19 (1H, d, J = 1.6 Hz, H-1″), 4.03 (1H, dd, J = 3.5, 1.8 Hz, H-2″), 3.88 (1H, dd, J = 3.5, 9.5 Hz, H-3″), 3.48 (1H, t, J = 9.5 Hz, H-4″), 3.73 (1H, dd, J = 10.2, 6.3 Hz, H-5″), 1.23 (3H, d, J = 6.0 Hz, H-6″); caffeoyl moiety δ 7.06 (1H, d, J = 2.0 Hz, H-2‴), 6.78 (1H, d, J = 8.2 Hz, H-5‴), 6.95 (1H, dd, J = 8.2, 2.0 Hz, H-6‴), 6.36 (1H, d, J = 15.9 Hz, H-α), 7.65 (1H, d, J = 15.9 Hz, H-β); ^{13}C NMR (CD_3-OD, 90 MHz) (Table 1); HRFABMS m/z 671.2189 $[M + H]^+$, 693 $[M + Na]^+$, (calcd for $C_{30}H_{39}O_{17}$, 671.2187).

Gmelinoside E (6): obtained as a white amorphous powder (76 mg); $[\alpha]^{25}_D$ −116.8° (c 0.43, MeOH); UV (MeOH) λ_{max} (log ϵ) 216 (4.21), 228 (4.12), 245 (4.18), 279 (4.27), 310 (4.33) nm; IR (KBr) ν_{max} 3460 (OH), 1695 (C═O), 1630 (C═C), 1650 (C═C iridoid), 1590 (aromatic) cm^{-1}; ^{1}H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.07 (1H, d, J = 9.5 Hz, H-1), 6.53 (1H, dd, J = 6.0, 1.7 Hz, H-3), 5.10 (1H, dd, J = 6.0, 4.3 Hz, H-4), 2.46 (1H, m, H-5), 4.11 (1H, dd, J = 8.2, 1.7 Hz, H-6), 3.65 (1H, s, H-7), 2.65 (1H, dd, J = 9.5, 8.2 Hz, H-9), 4.81 (1H, d, J = 12.5 Hz, H-10A), 5.69 (1H, d, J = 12.5 Hz, H-10B); glucosyl moiety δ 4.79 (1H, d, J = 7.8 Hz, H-1′), 3.28 (1H, dd, J = 7.8, 9.1 Hz, H-2′), 3.45 (1H, t, J = 9.0 Hz, H-3′), 3.28 (1H, t, J = 9.0 Hz, H-4′), 3.29 (1H, m, H-5′), 3.77 (1H, dd, J = 11.8, 5.7 Hz, H-6′A), 3.85 (1H, dd, J = 11.8, 2.0 Hz, H-6′B); rhamnosyl moiety δ 5.12 (1H, d, J = 1.7 Hz, H-1″), 5.43 (1H, dd, J = 3.5, 1.8 Hz, H-2″), 3.97 (1H, dd, J = 3.5, 9.5 Hz, H-3″), 4.92 (1H, t, J = 9.6 Hz, H-4″), 3.82 (1H, dd, J = 10.2, 6.2 Hz, H-5″), 1.22 (3H, d, J = 6.2 Hz, H-6″); feruloyl moiety δ 7.19 (1H, d, J = 2.0 Hz, H-2‴), 6.92 (1H, d, J = 8.5 Hz, H-5‴), 7.06 (1H, dd, J = 8.5, 1.8 Hz, H-6‴), 6.43 (1H, d, J = 15.9 Hz, H-α), 7.69 (1H, d, J = 15.9 Hz, H-β), 3.89 (3H, s, OMe), 1.88, 2.03 (each 3H, s, OAc); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS m/z 769.2558 $[M + H]^+$, 791 $[M + Na]^+$, 231 [diacetylrhamnose-oxonium]$^+$ ion, 177 [feruloyl]$^+$ (calcd for $C_{35}H_{45}O_{19}$, 769.2555).

Gmelinoside F (7): obtained as a white amorphous powder (50 mg); $[\alpha]^{25}_D$ −162.2° (c 0.74, MeOH); UV (MeOH) λ_{max} (log ϵ) 233 (4.64), 258 (4.58), 272 (4.45), 302 (sh 4.64), 327 (4.23) nm; IR (KBr) ν_{max} 3370 (OH), 1725 (C═O), 1630 (C═C), 1658 (C═C iridoid), 1530 (aromatic), cm^{-1}; ^{1}H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.09 (1H, d, J = 9.2 Hz, H-1), 6.40 (1H, dd, J = 6.0, 2.0 Hz, H-3), 5.12 (1H, dd, J = 6.0, 4.5 Hz, H-4), 2.50 (1H, m, H-5), 4.07 (1H, dd, J = 8.0, 1.5 Hz, H-6), 3.70 (1H, s, H-7), 2.71 (1H, dd, J = 9.2, 8.0 Hz, H-9), 4.74 (1H, d, J = 12.9 Hz, H-10A), 5.83 (1H, d, J = 12.9 Hz, H-10B); glucosyl moiety δ 4.86 (1H, d, J = 8.0 Hz, H-1′), 3.49 (1H, dd, J = 8.0, 9.5 Hz, H-2′), 3.71 (1H, t, J = 9.5 Hz, H-3′), 3.49 (1H, t, J = 9.5 Hz, H-4′), 3.24 (1H, m, H-5′), 4.18 (1H, dd, J = 11.9, 6.7 Hz, H-6′A), 4.39 (1H, dd, J = 11.9, 2.0 Hz, H-6′B); rhamnosyl moiety δ 5.14 (1H, d, J = 1.8 Hz, H-1″), 3.78 (1H, dd, J = 3.3, 1.8 Hz, H-2″), 3.69 (1H, dd, J = 3.3, 9.5 Hz, H-3″), 3.40 (1H, t, J = 9.3 Hz, H-4″), 3.87 (1H, dd, J = 10.0, 6.2 Hz, H-5″), 1.21 (3H, d, J = 6.3 Hz, H-6″); p-OH-benzoyl moiety δ 7.93 (2H, d, J = 8.8 Hz, H-2‴, 6‴), 6.98 (1H, d, J = 8.8 Hz, H-3‴), 7.28 (1H, d, J = 8.4 Hz, H-5‴), 2.10 (3H, s, OAc); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS m/z 671.2192 $[M + H]^+$, 693 $[M + Na]^+$, 138, 121, 93, and 65 (calcd for $C_{30}H_{39}O_{17}$, 671.2187).

Gmelinoside G (8): obtained as a colorless amorphous powder (66 mg); $[\alpha]^{25}_D$ −146.9° (c 1.01, MeOH); UV (MeOH) λ_{max} (log ϵ) 225 (4.49), 328 (4.58) nm; IR (KBr) ν_{max} 3450 (OH), 1718 (C═O), 1638 (C═C), 1650 (C═C iridoid), 1545 (aromatic) cm^{-1}; ^{1}H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.00 (1H, d, J = 9.4 Hz, H-1), 6.41 (1H, dd, J = 6.5, 1.8 Hz, H-3), 5.13 (1H, dd, J = 6.5, 4.5 Hz, H-4), 2.59 (1H, m, H-5), 4.08 (1H, dd, J = 8.5, 1.8 Hz, H-6), 3.66 (1H, s, H-7), 2.67 (1H, dd, J = 9.4, 7.8 Hz, H-9), 3.84 (1H, d, J = 13.2 Hz, H-10A), 4.05 (1H, d, J = 13.2 Hz, H-10B); glucosyl moiety δ 4.87 (1H, d, J = 8.1 Hz, H-1′), 3.37 (1H, dd, J = 8.1, 9.5 Hz, H-2′), 3.26 (1H, t, J = 9.5 Hz, H-3′), 3.43 (1H, t, J = 10.1 Hz, H-4′), 3.40 (1H, m, H-5′), 3.72 (1H, dd, J = 11.6, 6.5 Hz, H-6′A), 3.90 (1H, dd, J = 11.6, 2.2 Hz, H-6′B); rhamnosyl moiety δ 5.10 (1H, d, J = 1.9 Hz, H-1″), 5.33 (1H, dd, J = 3.5, 1.9 Hz, H-2″), 4.98 (1H, dd, J = 3.5, 9.5 Hz, H-3″), 3.55 (1H, t, J = 9.5 Hz, H-4″), 3.71 (1H, dd, J = 10.0, 6.2 Hz, H-5″), 1.38 (3H, d, J = 6.5 Hz, H-6″); feruloyl moieties δ 7.21 (1H, d, J = 1.8 Hz, H-2‴), 6.79 (1H, d, J = 8.5 Hz, H-5‴), 7.10 (1H, dd, J = 8.5, 1.8 Hz, H-6‴), 6.46 (1H, d, J = 16.0 Hz, H-α), 7.57 (1H, d, J = 16.0 Hz, H-β), 7.18 (1H, d, J = 2.0 Hz, H-2⁗), 6.88 (1H, d, J = 8.0 Hz, H-5⁗), 6.92 (1H, dd, J = 8.0, 2.0 Hz, H-6⁗), 6.32 (1H, d, J = 16.5 Hz, H-α), 7.38 (1H, d, J = 16.5 Hz, H-β), 3.90, 3.78 (6H, s, OMe); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS m/z 861.2821 $[M + H]^+$, 883 $[M + Na]^+$, 500 [diferuloylrhamnose-oxonium]$^+$ ion (calcd for $C_{41}H_{49}O_{20}$, 861.2816).

Gmelinoside H (9): obtained as an amorphous powder (71 mg); $[\alpha]^{25}_D$ −166.2° (c 0.58, MeOH); UV (MeOH) λ_{max} (log ϵ) 229 (4.24), 301 (4.06), 334 (4.43) nm;

IR (KBr) ν_{max} 3455 (OH), 1705 (C=O), 1635 (C=C), 1668 (C=C iridoid), 1535 (aromatic) cm^{-1}; ^1H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.16 (1H, d, J = 9.5 Hz, H-1), 6.33 (1H, dd, J = 6.0, 1.2 Hz, H-3), 5.18 (1H, dd, J = 6.0, 4.0 Hz, H-4), 2.45 (1H, m, H-5), 4.06 (1H, dd, J = 8.2, 1.5 Hz, H-6), 3.75 (1H, s, H-7), 2.60 (1H, dd, J = 9.5, 7.9 Hz, H-9), 3.92 (1H, d, J = 13.3 Hz, H-10A), 4.29 (1H, d, J = 13.3 Hz, H-10B); glucosyl moiety δ 4.99 (1H, d, J = 8.0 Hz, H-1′), 3.27 (1H, dd, J = 8.0, 9.2 Hz, H-2′), 3.40 (1H, t, J = 9.2 Hz, H-3′), 3.32 (1H, t, J = 9.2 Hz, H-4′), 3.27 (1H, m, H-5′), 3.69 (1H, dd, J = 12.1, 6.5 Hz, H-6′A), 3.93 (1H, dd, J = 12.1, 2.1 Hz, H-6′B); rhamnosyl moiety δ 5.07 (1H, d, J = 1.8 Hz, H-1″), 5.42 (1H, dd, J = 3.5, 1.7 Hz, H-2″), 5.53 (1H, dd, J = 3.5, 9.2 Hz, H-3″), 4.98 (1H, t, J = 9.9 Hz, H-4″), 4.00 (1H, dq, J = 10.0, 6.5 Hz, H-5″), 1.18 (3H, d, J = 6.2 Hz, H-6″); feruloyl moieties δ 7.37 (1H, d, J = 2.1 Hz, H-2‴), 6.96 (1H, d, J = 8.0 Hz, H-5‴), 7.21 (1H, dd, J = 8.0, 2.1 Hz, H-6‴), 6.42 (1H, d, J = 15.9 Hz, H-α), 7.72 (1H, d, J = 15.9 Hz, H-β), 7.24 (1H, d, J = 2.1 Hz, H-2⁗), 6.91 (1H, d, J = 8.2 Hz, H-5⁗), 7.13 (1H, dd, J = 8.2, 1.8 Hz, H-6⁗), 6.35 (1H, d, J = 15.9 Hz, H-α), 7.67 (1H, d, J = 15.9 Hz, H-β), 3.93, 3.87 (6H, s, OMe), 1.96 (3H, s, OAc); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS m/z 903.2925 $[M + H]^+$, 925 $[M + Na]^+$, 541 [triacylrhamnose-oxonium]$^+$ ion (calcd for $C_{43}H_{51}O_{21}$, 903.2923).

Gmelinoside I (10): obtained as an amorphous powder (27 mg); $[\alpha]^{25}_D$ −106.2° (c 0.45, MeOH); UV (MeOH) λ_{max} (log ϵ) 235 (4.13), 302 (4.13), 328 (4.49) nm; IR (KBr) ν_{max} 3465 (OH), 1715 (C=O), 1630 (C=C), 1662 (C=C iridoid), 1528 (aromatic) cm^{-1}; ^1H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.14 (1H, d, J = 9.5 Hz, H-1), 6.44 (1H, dd, J = 6.3, 2.0 Hz, H-3), 5.21 (1H, dd, J = 6.3, 4.5 Hz, H-4), 2.55 (1H, m, H-5), 4.11 (1H, dd, J = 8.0, 1.5 Hz, H-6), 3.78 (1H, s, H-7), 2.64 (1H, dd, J = 9.6, 8.0 Hz, H-9), 3.80 (1H, d, J = 12.9 Hz, H-10A), 4.14 (1H, d, J = 12.9 Hz, H-10B); glucosyl moiety δ 4.63 (1H, d, J = 7.8 Hz, H-1′), 3.23 (1H, dd, J = 7.8, 8.8 Hz, H-2′), 3.39 (1H, t, J = 9.0 Hz, H-3′), 3.24 (1H, t, J = 9.0 Hz, H-4′), 3.29 (1H, m, H-5′), 3.67 (1H, dd, J = 11.7, 5.4 Hz, H-6′A), 3.86 (1H, dd, J = 11.7, 3.0 Hz, H-6′B); rhamnosyl moiety δ 5.09 (1H, d, J = 1.8 Hz, H-1″), 5.23 (1H, dd, J = 9.2, 3.5 Hz, H-2″), 4.08 (1H, dd, J = 3.5, 9.5 Hz, H-3″), 4.84 (1H, t, J = 9.5 Hz, H-4″), 3.94 (1H, dd, J = 9.5, 6.6 Hz, H-5″), 1.23 (3H, d, J = 6.1 Hz, H-6″); coumaroyl moieties δ 7.49 (2H, d, J = 8.6 Hz, H-2‴, 6‴), 6.76 (2H, d, J = 8.6 Hz, H-3‴, 5‴), 6.47 (1H, d, J = 16.5 Hz, H-α), 7.68 (1H, d, J = 16.5 Hz, H-β), 7.33 (2H, d, J = 8.6 Hz, H-2⁗, 6⁗), 6.65 (2H, d, J = 8.6 Hz, H-3⁗, 5⁗), 6.39 (1H, d, J = 16.5 Hz, H-α), 7.56 (1H, d, J = 16.5 Hz, H-β); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS m/z 801.2610 $[M + H]^+$, 823 $[M + Na]^+$; negative FABMS m/z 653 $[(M - H - 146]^-$, 507 $[(M - H) - 292]^-$ and 361 $[M - H - 438]^-$ (calcd for $C_{39}H_{45}O_{18}$, 801.2606).

Gmelinoside J (11): obtained as a white amorphous powder (16 mg); $[\alpha]^{25}_D$ −132.5° (c 0.38, MeOH); UV (MeOH) λ_{max} (log ϵ) 236 (4.43), 276 (3.78) nm; IR (KBr) ν_{max} 3535 (OH), 1698 (C=O), 1613 (C=C), 1658 (C=C iridoid), 1545 (aromatic) cm^{-1}; ^1H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.18 (1H, d, J = 9.5 Hz, H-1), 6.37 (1H, dd, J = 6.0, 1.9 Hz, H-3), 5.11 (1H, dd, J = 6.0, 4.5 Hz, H-4), 2.50 (1H, m, H-5), 4.09 (1H, dd, J = 8.0, 1.5 Hz, H-6), 3.70 (1H, s, H-7), 2.61 (1H, dd, J = 9.5, 7.9 Hz, H-9), 3.81 (1H, d, J = 13.5 Hz, H-10A), 4.17 (1H, d, J = 13.5 Hz, H-10B); glucosyl moiety δ 4.78 (1H, d, J = 8.0 Hz, H-1′), 3.26 (1H, dd, J = 7.8, 9.5 Hz, H-2′), 3.41 (1H, t, J = 9.5 Hz, H-3′), 3.28 (1H, t, J = 9.5 Hz, H-4′), 3.31 (1H, m, H-5′), 3.63 (1H, dd, J = 11.9, 6.8 Hz, H-6′A), 3.90 (1H, dd, J = 11.9, 2.3 Hz, H-6′B); rhamnosyl moiety δ 5.09 (1H, d, J = 2.1 Hz, H-1″), 5.53 (1H, dd, J = 3.8, 2.1 Hz, H-2″), 4.01 (1H, dd, J = 3.8, 9.8 Hz, H-3″), 5.38 (1H, t, J = 9.8 Hz, H-4″), 3.81 (1H, dq, J = 9.7, 6.0 Hz, H-5″), 1.26 (3H, d, J = 6.4 Hz, H-6″); benzoyl moieties δ 8.13 (2H, dd, J = 8.0, 1.0 Hz, H-2‴, 6‴), 7.41 (2H, t, J = 8.0 Hz, H-3‴, 5‴), 7.54 (1H, tt, J = 8.0 Hz, H-4‴), 8.08 (2H, dd, J = 8.0, 1.0 Hz, H-2⁗, 6⁗), 7.39 (2H, t, J = 8.0 Hz, H-3⁗, 5⁗), 7.49 (1H, tt, J = 8.0 Hz, H-4⁗); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HR-FABMS m/z 717.2398 $[M + H]^+$, 793 $[M + Na]^+$, 355 [dibenzylrhamnose-oxonium]$^+$ ion (calcd for $C_{35}H_{41}O_{16}$, 717.2384).

Gmelinoside K (12): obtained as a white amorphous powder (11 mg); $[\alpha]^{25}_D$ −140.2° (c 0.62, MeOH); UV (MeOH) λ_{max} (log ϵ) 236 (4.36), 276 (4.22) nm; IR (KBr) ν_{max} 3500 (OH), 1705 (C=O), 1625 (C=C), 1664 (C=C iridoid), 1585 (aromatic) cm^{-1}; ^1H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.12 (1H, d, J = 9.5 Hz, H-1), 6.46 (1H, dd, J = 6.0, 1.8 Hz, H-3), 5.12 (1H, dd, J = 6.2, 4.4 Hz, H-4), 2.67 (1H, m, H-5), 4.01 (1H, dd, J = 8.0, 1.6 Hz, H-6), 3.65 (1H, s, H-7), 2.59 (1H, dd, J = 9.5, 8.2 Hz, H-9), 3.98 (1H, d, J = 12.8 Hz, H-10A), 4.62 (1H, d, J = 12.8 Hz, H-10B); glucosyl moiety δ 4.98 (1H, d, J = 8.0 Hz, H-1′), 3.43 (1H, dd, J = 8.0, 9.1 Hz, H-2′), 3.49 (1H, t, J = 9.1 Hz, H-3′), 3.38 (1H, t, J = 9.1 Hz, H-4′), 3.12 (1H, m, H-5′), 3.65 (1H, dd, J = 11.7, 5.7 Hz, H-6′A), 3.88 (1H, dd, J = 11.7, 1.8 Hz, H-6′B), rhamnosyl moiety δ 5.19 (1H, d, J = 1.8 Hz, H-1″), 4.03 (1H, dd, J = 3.5, 1.8 Hz, H-2″), 5.38 (1H, dd, J = 3.5, 9.5 Hz, H-3″), 5.48 (1H, t, J = 9.5 Hz, H-4″), 3.63 (1H, dd, J = 10.2, 6.3 Hz, H-5″), 1.19 (3H, d, J = 6.2 Hz, H-6″); benzoyl moieties δ: 7.96 (2H, dd, J = 8.5, 1.2 Hz, H-2‴, 6‴), 7.47 (2H, t, J = 7.8 Hz, H-3‴, 5‴), 7.62 (1H, tt, J = 7.6 Hz, H-4‴), 7.85 (2H, dd, J = 8.5,1.2 Hz, H-2⁗, 6⁗), 7.45 (2H, t, J = 7.8 Hz, H-3⁗, 5⁗), 7.59 (1H, tt, J = 8.0 Hz, H-4⁗); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS m/z 717.2397 $[M + H]^+$, 793 $[M + Na]^+$, 355 [dibenzoylrhamnose-oxonium]$^+$ ion (calcd for $C_{35}H_{41}O_{16}$, 717.2394).

Gmelinoside L (13): obtained as an amorphous powder (59 mg); $[\alpha]^{25}_D$ −125.6° (c 0.80, MeOH); UV (MeOH) λ_{max} (log ϵ) 236 (4.68), 316 (4.63) nm; IR (KBr) ν_{max} 3380 (OH), 1725 (C=O), 1636 (C=C), 1665 (C=C iridoid), 1560 (aromatic) $cm^{-1;}$ ^1H NMR (CD_3OD, 600 MHz) aglycon moiety δ 5.08 (1H, d, J = 9.6 Hz, H-1), 6.39 (1H, dd, J = 6.0, 1.7 Hz, H-3), 5.11 (1H, dd, J = 6.0, 4.6 Hz, H-4), 2.47 (1H, m, H-5), 4.06 (1H, dd, J = 8.0, 1.7 Hz, H-6), 3.67 (1H, s, H-7), 2.58 (1H, dd, J = 9.6, 7.6 Hz, H-9), 3.82 (1H, d, J = 13.0 Hz, H-10A), 4.16 (1H, d, J = 13.0 Hz, H-10B); glucosyl moiety δ 4.78 (1H, d, J = 7.9 Hz, H-1′), 3.29 (1H, dd, J = 7.9, 9.3 Hz, H-2′), 3.43 (1H, t, J = 9.3 Hz, H-3′), 3.34 (1H, t, J = 9.1 Hz, H-4′), 3.25 (1H, m, H-5′), 3.66 (1H, dd, J = 11.9, 6.8 Hz, H-6′A), 3.92 (1H, dd, J = 11.9, 1.9 Hz, H-6′B); rhamnosyl moiety δ 5.02 (1H, d, J = 1.6 Hz, H-1″), 4.09 (1H, dd, J = 3.0, 1.6 Hz, H-2″), 5.29 (1H, dd, J = 3.0, 10.0 Hz, H-3″), 5.42 (1H, t, J = 10.0 Hz, H-4″), 4.00 (1H, dq, J = 10.0, 6.0 Hz, H-5″), 1.21 (3H, d, J = 6.2 Hz, H-6″); cinnamoyl moiety δ 7.69 (2H, d, J = 8.2 Hz, H-2‴, 6‴),

7.13 (2H, t, J = 8.2 Hz, H-3‴, 5‴), 7.34 (1H, m, H-4‴), 6.52 (1H, d, J = 16.0 Hz, H-α), 7.76 (1H, d, J = 16.0 Hz, H-*β*), 1.90 (3H, s, OAc); ^{13}C NMR (CD_3OD, 90 MHz) (Table 1); HRFABMS *m/z* 681.2402 $[M + H]^+$, 703 $[M + Na]^+$, 319 [acetylcinnamoylrhamnose-oxonium]$^+$ ion, 131 [cinnamoyl]$^+$ (calcd for $C_{32}H_{41}O_{16}$, 681.2395).

6-*O*-(3″-*O*-*trans*-Feruloyl)-α-L-rhamnopyranosylcatalpol (14): obtained as a white amorphous powder (15 mg); UV (MeOH) λ_{max} (log ϵ) 213 (3.91), 305 (4.08), 327 (4.29) nm; IR (KBr) ν_{max} 3378 (OH), 1690 (C=O), 1623 (C=C), 1650 (C=C iridoid), 1515 (aromatic) cm^{-1}; FABMS *m/z* 707 $[M + Na]^+$, 685 $[M + H]^+$, 323 [feruloylrhamnose-oxonium]$^+$ ion. Compound 14 was identified by comparison of spectral data with published values.[15]

6-*O*-(2″-Acetyl-3″,4″-*O*-di-*trans*-cinnamoyl)-α-L-rhamnopyranosylcatalpol (15): obtained as a white amorphous powder (12 mg); UV (MeOH) λ_{max} (log ϵ) 221 (4.48), 298 (4.75) nm; IR (KBr) ν_{max} 3410 (OH), 1718 (C=O), 1635 (C=C), 1665 (C=C iridoid), 1520 (aromatic) cm^{-1}; FABMS *m/z* 833 $[M + Na]^+$, 811 $[M + H]^+$, 449 [triacylrhamnose-oxonium]$^+$ ion, 131 [cinnamoyl]$^+$. Compound **15** was identified by comparison of spectral data with published values.[8]

Verbascoside: obtained as brownish amorphous powder (775 mg), and identified by TLC with an authentic sample and by comparison of spectral data with published values.[35]

Martynoside: obtained as pale beige amorphous powder (98 mg), and identified by TLC with an authentic sample and by comparison of spectral data with published values.[36]

Acetylation of Compounds 2, 3, 6, 8, and 9. Compounds **2**, **3**, and **6** (20 mg each) of **8** and **9** (10 mg each) were each treated with Ac_2O (1 mL) and pyridine (1 mL) at room temperature overnight. The reaction mixture was added to cold H_2O and was extracted with $CHCl_3$. The $CHCl_3$ extract was subjected to column chromatography over Si gel using C_6H_6–Me_2CO (9:1→7:3) to give compounds **2a**, **3a**, **6a**, **8a**, **9a**.

Gmelinoside A heptaacetate (2a): white amorphous powder; IR (KBr) ν_{max} 2948, 1752, 1630, 1580, 1510, 1460, 1100, 1036, 980, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.98, 2.02, 2.04, 2.07, 2.11, 2.13, and 2.18 (each 3H, s, OAc), aglycon moiety δ 5.12 (1H, d, J = 10 Hz, H-1), 6.30 (1H, dd, J = 6.0, 2.0 Hz, H-3), 5.18 (1H, dd, J = 6.0, 4.5 Hz, H-4), 2.51 (1H, m, H-5), 4.08 (1H, dd, J = 8.5, 1.5 Hz, H-6), 3.68 (1H, s, H-7), 2.73 (1H, dd, J = 9.8, 7.5 Hz, H-9), 4.66 (1H, d, J = 12.5 Hz, H-10A), 5.62 (1H, d, J = 12.5 Hz, H-10B), glucosyl moiety δ 5.02 (1H, d, J = 7.9 Hz, H-1′), 4.88 (1H, dd, J = 9.5, 8.0 Hz, H-2′), 5.21 (1H, t, J = 9.5 Hz, H-3′), 4.96 (1H, t, J = 9.5 Hz, H-4′), 3.32 (1H, m, H-5′), 4.18 (1H, dd, J = 12.0, 6.5 Hz, H-6′A), 4.32 (1H, dd, J = 12.0, 2.2 Hz, H-6′B), rhamnosyl moiety δ 5.09 (1H, d, J = 1.8 Hz, H-1″), 5.32 (1H, dd, J = 3.4, 1.8 Hz, H-2″), 5.40 (1H, dd, J = 10.1, 3.4 Hz, H-3″), 5.25 (1H, bt, J = 10.0 Hz, H-4″), 4.13 (1H, dq, J = 10.0, 6.0 Hz, H-5″), 1.23 (3H, d, J = 6.0 Hz, H-6″), cinnamoyl moiety δ 7.56 (2H, m, H-2‴, 6‴), 6.95 (2H, d, J = 8.5 Hz, H-3‴, 5‴), 7.44 (1H, m, H-4‴), 6.38 (1H, d, J = 16.0 Hz, H-α), 7.65 (1H, d, J = 16.0 Hz, H-*β*); FABMS *m/z* 955 $[M + Na]^+$, 933 $[M + H]^+$, 624 $[M + Na - 331]^+$ [2,3,4,6-*O*-tetraacetyl glucose oxonium]$^+$ ion, 682 $[M + Na - 273]^+$ [2,3,4-*O*-triacetylrhamnose-oxonium]$^+$ ion, 131 [cinnamoyl]$^+$.

Gmelinoside B pentaacetate (3a): white amorphous powder; IR (KBr) ν_{max} 2940, 1757, 1638, 1601, 1508, 1425, 1375, 1145, 1040 and 980, and 903 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.99, 2.02, 2.07, 2.10, 2.13, 2.15 and 2.19, (each 3H, s, OAc), aglycon moiety δ 5.11 (1H, d, J = 9.6 Hz, H-1), 6.41 (1H, dd, J = 6.0, 1.8 Hz, H-3), 5.16 (1H, dd, J = 6.5, 4.3 Hz, H-4), 2.55 (1H, m, H-5), 4.11 (1H, dd, J = 8.0, 1.0 Hz, H-6), 3.68 (1H, s, H-7), 2.66 (1H, dd, J = 9.5, 8.0 Hz, H-9), 4.70 (1H, d, J = 13.0 Hz, H-10A), 5.65 (1H, d, J = 13.0 Hz, H-10B), glucosyl moiety δ 5.01 (1H, d, J = 7.7 Hz, H-1′), 4.93 (1H, dd, J = 9.3, 7.9 Hz, H-2′), 5.13 (1H, t, J = 9.3 Hz, H-3′), 4.90 (1H, t, J = 9.3 Hz, H4′), 3.54 (1H, m, H-5′), 4.43 (1H, dd, J = 12.5, 6.8 Hz, H-6′A), 4.80 (1H, dd, J = 12.5, 2.0 Hz, H-6′B), rhamnosyl moiety δ 5.11 (1H, d, J = 1.7 Hz, H-1″), 5.36 (1H, dd, J = 3.5, 1.7 Hz, H-2″), 5.41 (1H, dd, J = 9.5, 3.5 Hz, H-3″), 5.22 (1H, t, J = 9.5 Hz, H-4″), 4.03 (1H, m, H-5″), 1.26 (3H, d, J = 6.5 Hz, H-6″), cinnamoyl moiety δ 7.52 (2H, m, H-2‴, 6‴), 6.88 (2H, d, J = 8.5 Hz, H-3‴, 5‴), 7.40 (1H, m, H-4‴), 6.35 (1H, d, J = 16.1 Hz, H-α), 7.76 (1H, d, J = 16.1 Hz, H-*β*); FABMS *m/z* 955 $[M + Na]^+$, 933 $[M + H]^+$ 624 $[M + Na - 331]^+$ [2,3,4,6-*O*-tetraacetylglucose-oxonium]$^+$ ion, 682 $[M + Na - 273]^+$ [2,3,4-*O*-triacetylrhamnose-oxonium]$^+$ ion, 131 [cinnamoyl]$^+$.

Gmelinoside E hexaacetate (6a): white amorphous powder; IR (KBr) ν_{max} 2943, 1752, 1630, 1600, 1509, 1420, 1370, 1128, 1048 and 981, and 908 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.98, 2.02, 2.05, 2.07, and 2.11, (each 3H, s, alcoholic Ac × 5), 2.32 (3H, s, phenolic Ac), aglycon moiety δ 4.82 (1H, d, J = 10.0 Hz, H-1), 6.39 (1H, dd, J = 6.5, 1.7 Hz, H-3), 5.19 (1H, dd, J = 6.0, 4.3 Hz, H-4), 2.51 (1H, m, H-5), 4.19 (1H, dd, J = 8.2, 1.5 Hz, H-6), 3.58 (1H, s, H-7), 2.62 (1H, dd, J = 9.8, 8.0 Hz, H-9), 4.87 (1H, d, J = 12.9 Hz, H-10A), 5.56 (1H, d, J = 12.9 Hz, H-10B), 3.91 (3H, s, OCH_3), glucosyl moiety δ 4.96 (1H, d, J = 8.0 Hz, H-1′), 4.69 (1H, dd, J = 9.0, 8.0 Hz, H-2′), 5.10 (1H, t, J = 9.0 Hz, H-3′), 4.76 (1H, t, J = 9.1 Hz, H-4′), 3.69 (1H, m, H-5′), 4.13 (1H, dd, J = 12.0, 4.9 Hz, H-6′A), 4.38 (1H, dd, J = 12.0, 2.5 Hz, H-6′B), rhamnosyl moiety δ 5.11 (1H, d, J = 1.8 Hz, H-1″), 5.33 (1H, dd, J = 3.5, 1.5 Hz, H-2″), 5.45 (1H, dd, J = 9.5, 3.5 Hz, H-3″), 4.97 (1H, t, J = 9.5 Hz, H-4″), 3.96 (1H, m, H-5″), 1.21 (3H, d, J = 6.3 Hz, H-6″), feruloyl moiety δ 7.22 (2H, m, H-2‴, 6‴), 7.08 (1H, d, J = 8.2 Hz, H-5‴), 6.55 (1H, d, J = 16.0 Hz, H-α), 7.66 (1H, d, J = 16.0 Hz, H-*β*); FABMS *m/z* 1043 $[M + Na]^+$, 1021 $[M + H]^+$, 712 $[M + Na - 331]^+$ [2,3,4,6-*O*-tetraacetylglucose-oxonium]$^+$ ion, 770 $[M + Na - 273]^+$ [2,3,4-*O*-triacetylrhamnose-oxonium]$^+$ ion, 219 [4-*O*-acetyl feruloyl]$^+$ and 177 [feruloyl]$^+$.

Gmelinoside G octaacetate (8a): white amorphous powder; IR (KBr) ν_{max} 2950, 1760, 1637, 1590, 1510, 1415, 1375, 1125, 1050 and 980 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.31, 2.27, 2.11, 2.07, 2.03, 2.01, 1.98, and 1.95 (each 3H, s, OAc), aglycon moiety δ 5.10 (1H, d, J = 9.5 Hz, H-1), 6.43 (1H, dd, J = 6.5, 2.0 Hz, H-3), 5.19 (1H, dd, J = 6.5, 4.5 Hz, H-4), 2.55 (1H, m, H-5), 4.18 (1H, dd, J = 8.5, 2.0 Hz, H-6), 3.68 (1H, s, H-7), 2.71 (1H, dd, J = 9.5, 8.0 Hz, H-9), 4.69 (1H, d, J = 12.8 Hz, H-10A), 5.42 (1H, d, J = 12.8 Hz, H-10B), glucosyl moiety δ 4.79 (1H, d, J = 8.0 Hz, H-1′), 4.80 (1H, dd, J

= 9.5, 8.0 Hz, H-2′), 4.96 (1H, t, J = 9.5 Hz, H-3′), 4.89 (1H, t, J = 9.5 Hz, H-4′), 3.32 (1H, m, H-5′), 4.23 (1H, dd, J = 11.5, 6.5 Hz, H-6′A), 4.32 (1H, dd, J = 11.5, 2.5 Hz, H-6′B), rhamnosyl moiety δ 5.01 (1H, d, J = 2.1 Hz, H-1″), 5.30 (1H, dd, J = 3.5, 1.7 Hz, H-2″), 4.68 (1H, dd, J = 9.6, 3.5 Hz, H-3″), 4.86 (1H, brt, J = 9.5 Hz, H-4″), 4.03 (1H, dq, J = 10.0, 6.5 Hz, H-5″), 1.27 (3H, d, J = 6.3 Hz, H-6″), feruloyl moieties δ 7.27 (1H, d, J = 2.3 Hz, H-2‴, 6‴), 7.12 (1H, d, J = 2.3 Hz, H-2⁗, 6⁗) 6.93 (1H, d, J = 8.5 Hz, 5‴), 6.81 (1H, d, J = 8.5 Hz, 5⁗), 6.42 (1H, d, J = 16.0 Hz, H-α), 6.38 (1H, d, J = 16.0 Hz, H-α), 7.55 (1H, d, J = 16.0 Hz, H-β), 7.40 (1H, d, J = 16.0 Hz, H-β), 3.82, 3,77 (6H, s, OCH_3); FABMS m/z 1219 $[M + Na]^+$, 1196 $[M + H]^+$, 888 $[M + Na - 331]^+$ [2,3,4,6-*O*-tetraacetylglucose-oxonium]$^+$ ion.

Gmelinoside H heptaacetate (9a): white amorphous powder; IR (KBr) ν_{max} 2948, 1765, 1635, 1597, 1510, 1420, 1365, 1130, 1055, and 983 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 2.36, 2.30, 2.16, 2.10, 2.08, 2.07, 1.95 and 1.92 (each 3H, s, OAc), aglycon moiety δ 5.19 (1H, d, J = 9.5 Hz, H-1), 6.38 (1H, dd, J = 6.0, 1.8 Hz, H-3), 5.20 (1H, dd, J = 6.0, 4.5 Hz, H-4), 2.45 (1H, m, H-5), 4.14 (1H, dd, J = 8.5, 1.8 Hz, H-6), 3.81 (1H, s, H-7), 2.78 (1H, dd, J = 9.5, 8.0 Hz, H-9), 4.82 (1H, d, J = 13.0 Hz, H-10A), 5.12 (1H, d, J = 13.0 Hz, H-10B), glucosyl moiety δ 4.95 (1H, d, J = 8.0 Hz, H-1′), 4.71 (1H, dd, J = 9.5, 8.0 Hz, H-2′), 4.95 (1H, t, J = 9.5 Hz, H-3′), 4.77 (1H, t, J = 9.5 Hz, H-4′), 3.60 (1H, m, H-5′), 4.13 (1H, dd, J = 12.5, 6.5 Hz, H-6′A), 4.54 (1H, dd, J = 12.5, 2.0 Hz, H-6′B), rhamnosyl moiety δ 5.08 (1H, d, J = 2.0 Hz, H-1″), 5.34 (1H, dd, J = 3.5, 1.7 Hz, H-2″), 5.44 (1H, dd, J = 9.5, 3.5 Hz, H-3″), 4.79 (1H, t, J = 9.5 Hz, H-4″), 4.09 (1H, dd, J = 10.0, 6.5 Hz, H-5″), 1.22 (3H, d, J = 6.5 Hz, H-6″), feruloyl moieties δ 7.34 (2H, d, J = 2.1 Hz, H-2‴, 6‴), 7.17 (2H, d, J = 2.1 Hz, H-2⁗, 6⁗) 6.98 (1H, d, J = 8.0 Hz, 5‴), 6.90 (1H, d, J = 8.0 Hz, 5⁗), 6.51 (1H, d, J = 16.2 Hz, H-α), 6.36 (1H, d, J = 16.2 Hz, H-α), 7.70 (1H, d, J = 16.2 Hz, H-β), 7.62 (1H, d, J = 16.2 Hz, H-β), 3.88, 3,82 (6H, s, OCH_3); FABMS m/z 1219 $[M + Na]^+$, 1196 $[M + H]^+$, 888 $[M + Na - 331]^+$ [2,3,4,6-*O*-tetraacetylglucose-oxonium]$^+$ ion.

Alkaline Hydrolysis of Compounds 4, 5, 7, 8 10, and 13. Each compound (5 mg) was treated with 1 mL 0.2 M methanolic NaOH for 5 h at room temperature with stirring under N_2, after which the reaction mixture was passed through a column filled with Amberlite IR-120B (H^+). The MeOH eluate was concentrated under reduced pressure and partitioned between EtOAc and H_2O. The compounds from the H_2O layers were co-identified with an authentic sample of 6-*O*-α-L-rhamnopyranosylcatalpol by TLC on Si gel, using $CHCl_3$−MeOH−H_2O (80:20:2) and EtOAc−MeOH−H_2O (100: 16.5:13.5) as solvents. The EtOAc layer obtained from the hydrolysis of compound **4** gave *p*-coumaric acid methyl ester, **5** gave caffeic acid methyl ester, **7** gave *p*-hydroxybenzoic acid methyl ester, **8** gave ferulic acid methyl ester, **10** gave *p*-coumaric acid methyl ester, and **13** gave cinnamic acid methyl ester, (TLC, Si gel, $CHCl_3$−MeOH (8.5: 1.5).

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