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Synthesis of Antioxidant Isoflavone Fatty Acid Esters[1]

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Abstract—LDL antioxidant mono- and dioleates and -stearates of the isoflavones genistein and daidzein are synthesised in high yield with excellent regioselectivity.

Introduction

It is widely acknowledged that the oxidation of Low Density Lipoprotein (LDL) plays an important role in the advancement of atherosclerosis.[2–4] It is known that circulating plasma LDL is protected against oxidation,[5] probably owing to the high concentration of water-soluble antioxidants present in plasma.[6] Oxidation of LDL, therefore, mainly occurs in the artery walls. Although LDL contains natural antioxidants such as tocopherols, β-carotene and ubiquinone,[7] these endogenous antioxidants are thought to contribute only about 30% to the prevention of oxidation.[8] It has hence been suggested that additional (exogenous) lipophilic antioxidants carried in LDL could be responsible for the remaining 70% of antioxidant activity. In connection with this, it has been shown that people consuming diets rich in soybean products have a lower incidence of cardiovascular disease.[9] This is thought to be due to soybeans being rich in phytoestrogen compounds, especially the isoflavones genistein and daidzein. In vitro studies have in fact shown that both genistein and daidzein are potent antioxidants.[10–12] Unfortunately, neither genistein nor daidzein, in their aglycone form, are likely to be considered as being responsible for any of the unaccounted for antioxidant activity of LDL due to their low lipophilicity. We have reported[13] that the intake of soy-derived isoflavones resulted in a reduced susceptibility of LDL particles to oxidation despite the fact that only trace amounts of isoflavones could be detected in the LDLs. However, in view of reports suggesting that endogenous human estrogens are present in lipoproteins as fatty acid esters,[14–18] it seemed possible that phytoestrogens such as genistein and daidzein could also undergo esterification in vivo. It is easily envisaged that such compounds could be responsible for the additional antioxidant activity.

We now present the first chemical synthesis of these isoflavone fatty acid esters. The method is both high yielding and regioselective, producing the 7-mono-, 4′-mono- or 7,4′-distearates and oleates of both genistein and daidzein at will.

Our recent results show that fatty acid esters of both genistein and daidzein have antioxidant properties and are readily incorporated into LDL particles in vitro.[19]

Results and Discussion

We have shown earlier that in compounds such as genistein **1** and daidzein **2**, the 7-OH exhibits a hundred fold acidity compared to the 4′-hydroxy group (CAMEO[20] calculated values) which can be exploited in selective mono-*O*-alkylations of these isoflavones.[21] Rapid reaction of a 7-phenolate from **1** or **2** and one equivalent of potassium *t*-butoxide in DMF with an acyl chloride (1 equiv.) yielded the isoflavone 7-mono fatty acid esters in high yields, with the isoflavone 7,4′-diesters being formed as minor products (Table 1). The corresponding 4′-monoesters were not produced under these conditions. For a selective synthesis of the isoflavone 4′-monoesters, the 7,4′-diphenolates were prepared by reaction of the isoflavone aglycone with 2.2–3.3 equiv. of base. The greater nucleophilicity of the 4′-phenolate compared to the 7-phenolate resulted in a selective reaction with acyl chlorides (1 equiv.) producing the isoflavone 4′ fatty acid

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Table 1. Results from the synthesis of genistein and daidzein stearates and oleates, **3**–**14**

Isoflavone (0.4 mmols)	Base (mmols)	Acyl chloride (mmols)	Major product	Yield %
Daidzein	0.4	Stearoyl (0.44)	**3**	82
Daidzein	0.88	Stearoyl (0.4)	**4**	76
Daidzein	0.88	Stearoyl (0.88)	**5**	90
Genistein	0.4	Stearoyl (0.44)	**6**	84
Genistein	1.32	Stearoyl (0.4)	**7**	77
Genistein	1.32	Stearoyl (0.8)	**8**	96
Daidzein	0.4	Oleoyl (0.44)	**9**	81
Daidzein	0.88	Oleoyl (0.4)	**10**	79
Daidzein	0.88	Oleoyl (0.88)	**11**	92
Genistein	0.4	Oleoyl (0.44)	**12**	87
Genistein	1.32	Oleoyl (0.4)	**13**	80
Genistein	1.32	Oleoyl (0.8)	**14**	95

esters. Again yields were high and the corresponding 7-monoesters were not formed in these reactions.

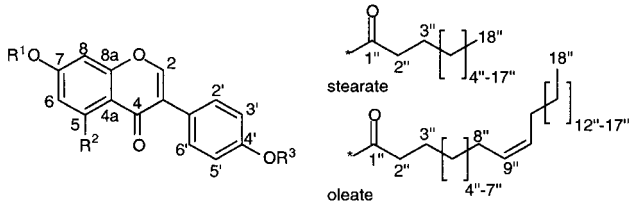
Finally, using an excess of base and acyl chloride, isoflavone 7,4′-diesters were obtained in high yields. The hydrogen-bond stabilised 5-hydroxy group in genistein did not react at 30°C, thus allowing genistein 7,4′-diesters to be produced in preference to genistein 5,7,4′-triesters.

Characterisation

The determination of the site of reaction in the polyhydroxyisoflavones genistein and daidzein was carried out by NMR, showing substantial downfield shifts for the aromatic protons *ortho* to OH upon acylation (Tables 2 and 3). For example, the esterification of the 7-hydroxy group of daidzein results in the H-8 doublet and H-6 doublet of

Table 2. ^{1}H NMR of daidzein and genistein stearates. 200 MHz, $CDCl_3$, *J* in Hz. Compound numbers correspond to Fig. 1. The two-prime signals refer to both acyl chains of the diesters

Proton	Compound **3**	**4**	**5**	**6**	**7**	**8**
2	8.0 (s)	8.0 (s)	8.0 (s)	7.9 (s)	7.8 (s)	7.8 (s)
5	8.3 (d) *8.8*	8.3 (d) *8.6*	8.3 (d) *8.4*			
6	7.2 (dd) *8.8*, *2.0*	6.9 (dd) *8.6*, *2.2*	7.2 (dd) *8.4*, *2.2*	6.7 (d) 2.0	6.3 (d) *2.2*	6.6 (d) *2.1*
8	7.3 (d) *2.0*	6.9 (d) *2.2*	7.3 (d) *2.2*	6.6 (d) *2.2*	6.2 (d) *2.2*	6.8 (d) *2.1*
2′, 6′	7.4 (d) *8.4*	7.6 (d) *8.8*	7.4 (d) *8.0*	7.4 (d) *8.8*	7.5 (d) *8.4*	7.5 (d) *8.4*
3′, 5′	6.9 (d) *8.4*	7.2 (d) *8.8*	6.8 (d) *8.0*	6.9 (d) *8.8*	7.2 (d) *8.4*	7.2 (d) *8.4*
2″	2.6 (t) *7.4*	2.6 (t) *7.4*	2.6 (t) *7.8*	2.6 (t) *7.4*	2.6 (t) *7.4*	2.6 (t) *7.7*
3″	1.8 (m)	1.8 (m)	1.8 (m)	1.8 (m)	1.8 (m)	1.8 (m)
4″–17″	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)
18″	0.9 (t) *6.2*	0.9 (t) *6.2*	0.9 (t) *6.3*	0.9 (t) *6.3*	0.9 (t) *6.3*	0.9 (t) *6.8*



R^1=R^2=R^3=H Daidzein **1**
R^1=R^3=H, R^2=OH Genistein **2**
R^1=$CO(CH_2)_{16}CH_3$, R^2=R^3=H Daidzein 7-stearate **3**
R^1=R^2=H, R^3=$CO(CH_2)_{16}CH_3$ Daidzein 4′-stearate **4**
R^1= R^3=$CO(CH_2)_{16}CH_3$, R^2=H Daidzein 4′,7- distearate **5**
R1=$CO(CH_2)_{16}CH_3$, R^2=OH, R^3=H Genistein 7-stearate **6**
R^1=H, R^2=OH, R^3=$CO(CH_2)_{16}CH_3$ Genistein 4′-stearate **7**
R^1=R^3=$CO(CH_2)_{16}CH_3$, R^2=OH Genistein 4′,7-distearate **8**
R^1=$CO(CH_2)_7CH$=$CH(CH_2)_7CH_3$, R^2= R^3=H Daidzein 7-oleate **9**
R^1=R^2=H, R^3=$CO(CH_2)_7CH$=$CH(CH_2)_7CH_3$ Daidzein 4′-oleate **10**
R^1=R^3=$CO(CH_2)_7CH$=$CH(CH_2)_7CH_3$, R^2=H Daidzein 4′,7-dioleate **11**
R^1=$CO(CH_2)_7CH$=$CH(CH_2)_7CH_3$, R^2=OH, R^3=H Genistein 7-oleate **12**
R^1=H, R^2=OH, R^3=$CO(CH_2)_7CH$=$CH(CH_2)_7CH_3$ Genistein 4′-oleate **13**
R^1=R^3=$CO(CH_2)_7CH$=$CH(CH_2)_7CH_3$, R^2=OH Genistein 4′,7-dioleate **14**

Figure 1. Structures of isoflavone aglycones genistein and daidzein, and isoflavone mono- and distearates and oleates synthesised.

Table 3. ^{1}H NMR of daidzein and genistein oleates. TMS internal standard, 200 MHz, $CDCl_3$, *J* in Hz. Compound numbers correspond to Fig. 1. The two-prime signals refer to both acyl chains of the diesters

Proton	Compound **9**	**10**	**11**	**12**	**13**	**14**
2	8.0 (s)	7.9 (s)	8.0 (s)	7.9 (s)	7.9 (s)	8.0 (s)
5	8.3 (d) *8.6*	8.2 (d) *8.8*	8.3 (d) *8.8*			
6	7.2 (dd) *8.6, 2.2*	6.9 (dd) *8.8, 2.0*	7.2 (dd) *8.8, 2.2*	6.7 (d) *2.0*	6.3 (d) *2.2*	6.8 (d) *2.2*
8	7.3 (d) *2.2*	6.9 (d) *2.0*	7.3 (d) *2.2*	6.6 (d) *2.0*	6.3 (d) *2.2*	6.6 (d) *2.2*
2′, 6′	7.4 (d) *8.4*	7.6 (d) *8.4*	7.6 (d) *8.8*	7.4 (d) *8.8*	7.5 (d) *8.4*	7.6 (d) *8.4*
3′, 5′	6.9 (d) *8.4*	7.1 (d) *8.4*	7.1 (d) *8.8*	6.9 (d) *8.8*	7.2 (d) *8.4*	7.2 (d) *8.4*
2″	2.6 t *7.6*	2.5 t *7.6*	2.6 (m)	2.6 (t) *7.8*	2.6 t *7.8*	2.6 t *7.3*
3″	1.7 (m)	1.7 (m)	1.8 (m)	1.7 (m)	1.8 (m)	1.8 (m)
4″–17″	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)
18″, 11″	2.0 (m)	2.0 (m)	2.0 (m)	2.0 (m)	2.0 (m)	2.0 (m)
9″, 10″	5.3 (m)	5.3 (m)	5.4 (m)	5.4 (m)	5.4 (m)	5.4 (m)
12″–17″	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)	1.3 (m)
18″	0.9 (t) *6.2*	0.9 (t) *6.2*	0.9 (t) *6.6*	0.9 (t) *7.0*	0.9 (t) *6.6*	0.9 (t) *6.6*

doublets moving downfield by 0.5 and 0.3 ppm respectively when compared to the values for daidzein. The 3′,5′ doublet is virtually unchanged. Acylation at the 4′-*O*-position shows downfield shifts (0.3 ppm) for the 3′,5′ and 2′,6′ doublets compared to free daidzein, whereas H-6 and H-8 are unaffected. Diesters show the relevant shifts in both the A and B rings of the molecule. The existence of a free hydroxy group at the 5 position in genistein is confirmed by the presence of an OH signal at δ 12.5 as in unesterified genistein. A thorough 2D ^{13}C NMR analysis of the fatty acid esters allowed the assignment of all carbon atoms (Tables 4 and 5) with the exception of those embedded in the aliphatic chains at the γ site or farther from the carbonyl or chain terminus, or the β site or farther from the oleate C═C. Thus in the ^{13}C NMR of the stearates, C-4″ to C-15″ overlap while in the oleates the signals of C-4″ to C-7″ appear together with those of C-12″ to C-15″. In the diesters the respective signals from the two aliphatic chains are indistinguishable expect for the carbonyl α-CH_2 signals ($\Delta\delta$ 0.1 ppm) in the proton spectra. The availability of diacyl and different monoacyl derivatives makes it possible to differentiate between the ester carbonyls by ^{13}C NMR spectra. An acyl carbon at the 7-*O* site always resonates at a higher field than one at the 4′-*O* site. Typical values are δ 171.5 and 172.5 for the former and the latter, respectively. In IR the fatty acid esters show two carbonyl absorptions, at 1740–1760 and 1640–1650 cm^{-1} corresponding to the ester and ketone carbonyls, respectively.

Fig. 2 shows the X-ray structure of **8**. Two structural features are apparent. First, the structure is completely linear with no folding of the fatty acid chains. Packing is by van der Waals bonding. Second, there is evidence of the partial enolic nature of the keto group (Table 6). The C═O bond (C4–O2) in **8** is 1.255 (7) Å as compared to 1.239 in daidzein.[22] At the same time the C-5/OH bond in **8** is 1.346(7) Å whereas in daidzein the C-7/OH bond is 1.359 Å (Table 6).

Table 4. ^{13}C NMR of daidzein and genistein stearates. 50 MHz for compounds **3**, **4**, **5**, **7** and 125 MHz for **6**, **8**. The two-prime signals refer to both acyl chains of the diesters

Carbon	Compound **3**	**4**	**5**	**6**	**7**	**8**
2	152.7	152.6	153.2	153.4	153.2	153.8
3	123.1	124.2	124.9	122.6	123.1	123.7
4	176.1	176.1	175.5	181.4	180.4	181.0
5	127.8	129.4	129.1	162.5	157.9	162.5
6	119.5	115.8	119.7	105.5	99.7	105.6
7	156.7	163.4	154.8	156.2	162.7	156.3
8	110.9	102.6	110.0	100.9	94.2	101.0
4a	122.2	117.8	122.3	109.5	115.6	109.4
8a	156.7	158.5	156.7	157.0	162.3	156.9
1′	125.4	121.9	127.9	124.1	128.3	127.9
2′, 6′	130.2	130.1	130.0	130.3	130.0	130.0
3′, 5′	115.4	121.6	121.8	115.7	121.8	121.9
4′	154.6	152.3	150.9	156.2	150.8	151.1
1″	171.5	173.6	171.4, 172.3	171.5	172.8	171.2, 172.2
2″	35.5	35.4	34.5	34.5	34.5	34.5
3″	25.2	25.2	24.8	24.8	24.9	24.8, 25.0
4″–15″	29.1–29.7	29.4–29.7	29.1–29.7	29.4–30.0	29.1–29.7	29.1–29.7
16″	31.9	32.0	32.0	32.0	31.9	32.0
17″	22.7	22.7	22.7	22.7	22.7	22.7
18″	14.1	14.1	14.1	14.1	14.1	14.1

Table 5. ^{13}C NMR of daidzein and genistein oleates. 50 MHz for compounds **9**, **12**, **13**, **14** and 125 MHz for **10**, **11**. The two-prime signals refers to both acyl chains of the diesters

Carbon	Compound					
	9	**10**	**11**	**12**	**13**	**14**
2	152.8	153.1	153.2	153.8	153.1	153.9
3	122.0	127.9	124.8	122.5	123.1	123.7
4	176.2	176.3	175.5	181.2	180.3	181.0
5	127.7	129.4	127.8	162.2	157.8	162.4
6	119.5	115.6	119.7	105.3	99.6	105.6
7	156.1	162.1	154.7	156.1	162.8	156.2
8	110.8	102.8	110.9	100.9	94.0	100.9
4a	123.1	117.6	122.2	109.7	115.3	109.4
8a	156.6	158.1	156.7	156.8	162.1	156.9
1′	125.3	124.2	129.1	124.3	128.1	127.8
2′, 6′	130.1	130.1	130.0	130.0	129.9	129.7
3′, 5′	115.6	121.7	121.7	115.5	121.7	121.9
4′	154.5	150.7	150.9	156.2	150.7	151.1
1″	171.4	172.6	171.4, 172.2	171.7	172.3	171.2, 172.2
2″	34.4	34.4	34.4	34.4	34.4	34.4
3″	24.7	25.3	24.8. 24.9	24.7	24.9	24.8, 24.9
4″–7″	29.0–29.7	29.2–30.0	29.1–29.7	29.0–29.7	29.1–29.7	29.1–29.8
12″–15″						
8″, 11″	27.2 & 27.1	29.1	27.2	27.2	27.2	27.2
9″, 10″	130.5	129.7	129.6	130.1	129.6	130
16″	31.9	31.9	31.9	31.9	31.9	31.9
17″	22.7	22.7	22.7	22.7	22.7	22.7
18″	14.1	14.1	14.1	14.1	14.1	14.1

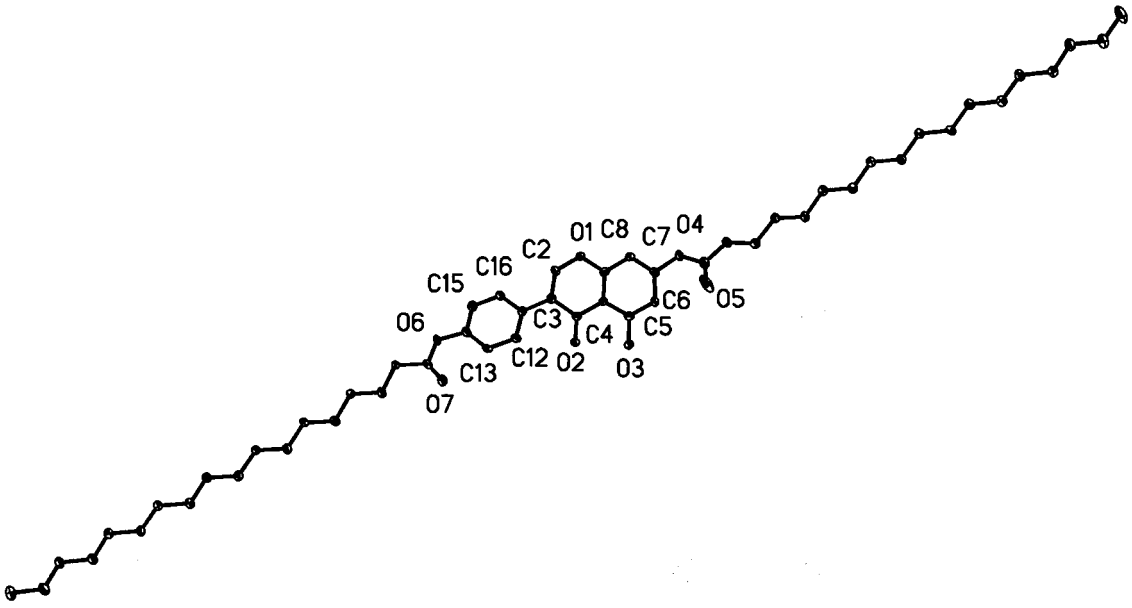


Figure 2. View of genistein-7,4′-distearate **8**. Thermal ellipsoids at 30% probability level. Enolic oxygen O3 (C5–O3 1.346(/)Å) forms an internal hydrogen bond with keto oxygen O2 (C4–O2 1.255(7) Å), the O2…O3 distance being 2.544 Å, O2…H3A distance 1.789 and O3–H3A–O2 angle 148.6°.

Table 6. Selected bond lengths [A] and angles [deg] for **8**

O(1)–C(2)	1.350(7)	O(3)–C(5)–C(6)	119.9(6)
O(1)–C(10)	1.362(7)	O(3)–C(5)–C(9)	119.4(5)
C(4)–O(2)	1.255(7)	C(8)–C(7)–O(4)	114.5(5)
C(5)–O(3)	1.346(7)	C(6)–C(7)–O(4)	122.2(5)
C(7)–O(4)	1.385(7)	O(1)–C(10)–C(8)	116.8(5)
C(14)–O(6)	1.411(7)	O(1)–C(10)–C(9)	120.3(5)
O(6)–C(18)	1.351(7)	C(15)–C(14)–O(6)	117.0(6)
C(18)–O(7)	1.182(8)	C(13)–C(14)–O(6)	120.4(6)
O(4)–C(37)	1.356(8)	C(18)–O(6)–C(14)	121.1(5)
C(37)–O(5)	1.193(8)	O(7)–C(18)–O(6)	124.1(6)
		C(37)–O(4)–C(7)	122.9(5)
O(2)–C(4)–C(9)	122.0(5)	O(5)–C(37)–O(4)	121.8(6)
O(2)–C(4)–C(3)	122.9(5)		

Experimental

NMR spectra were recorded on a Varian Gemini 2000 or Bruker Avance 500 spectrometers. IR spectra were recorded on a Perkin–Elmer One FTIR instrument on KBr disks. UV spectra were recorded on a Cary SE UV-VIS-NIR spectrophotometer in 96% EtOH. Mass spectra were measured on a JEOL JMS SX102 mass spectrometer. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected.

X-ray crystal structure analysis

Crystal data for 8. ($C_{51}H_{76}O_7$) M=801.12, monoclinic $P2_1$ (no. 4), a=7.9820(16), b=7.2590(15), c=39.700(8) Å, β=93.93(3)°, V=2294.9(8) Å^3, Z=2, D_c=1.159 gcm^{-3}, T=193(1) K, μ(Cu–K$_\alpha$)=0.589 mm^{-1}, $F(000)$=876, R_1=0.0727, wR_2=0.1796 with $I>2\sigma(I)$, S=1.000, 4628 data collected, 2595 $I>2\sigma$ (I), 524 parameters.

A colorless crystal with dimensions of 0.40×0.20×0.08mm was mounted to the glass fiber using the oil-drop method.[23] The data was collected using CAD4 diffractometer, graphite monochromatized Cu–K$_\alpha$ radiation (λ=1.54178 Å), in $\omega-2\theta$-mode. Data reduction was done using the XCAD package.[24] The intensity data were corrected for Lorentz and polarization effects and for absorption and extinction. The structure was solved using direct methods. All non-H atoms were refined anisotropically. H atoms were refined using a riding model. The final difference Fourier map had peak maxima of 0.345 and minima −0.458 eÅ^{-3}. Programs from the Siemens SHELXTL-package[25] and SHELXL-97[26] were used for the solution, refinement and graphical representation of the structure. Full crystallographic data has been deposited at Cambridge Crystallographic Data Centre and is available as supplementary information.

Synthetic procedure

A solution of isoflavone (0.4 mmol) and *t*-BuOK (see Table 1 for mmol) in dry DMF (15 ml) is stirred at 30°C for 2.5 h under Ar. The fatty acid chloride (see Table 1 for mmol) in DMF (2 ml) is added to this solution and the reaction continued for 2.5 h. Pouring into ice water followed by extraction with ether/ethyl acetate (1/1), washing with aqueous $NaHCO_3$, drying and removal of solvent under reduced pressure gives the crude product. Purification by flash chromatography (silica, $CHCl_3$/MeOH, 95/5) yields the isoflavone fatty acid ester. For ^{1}H NMR of the stearates, see Table 2. For ^{1}H NMR of the oleates, see Table 3. For ^{13}C NMR of the stearates, see Table 4, and for ^{13}C NMR of the oleates, see Table 5.

Daidzein-7-monostearate 3. 82%; white solid (acetone) mp 136–38°C; UV nm (log ϵ) 260, (4.4), 307 (3.9); IR 3442, 1749 and 1640 cm^{-1}; HRMS calc. for $C_{33}H_{44}O_5$ 520.3182, found 520.3189; m/z 520 (M$^+$), 254 (100%).

Daidzein-4′-monostearate 4. 76%; white solid (acetone); mp 128–129°C; UV nm (log ϵ) 253 (4.4), 297 (4.0); IR 3322, 1736 and 1643 cm^{-1}; HRMS calc. for $C_{33}H_{44}O_5$ 520.3182, found 520.3189; m/z 520 (M$^+$), 254 (100%).

Daidzein-7,4′-distearate 5. 90%; white solid (acetone); mp 99–101°C; UV nm (log ϵ) 252 (4.6), 304 (3.9); IR 1748 and 1646 cm^{-1}; HRMS calc. for $C_{51}H_{78}O_6$ 786.5798, found 786.5789; m/z 786 (M$^+$), 520 (15%), 254 (100%).

Genistein-7-monostearate 6. 84%; white solid (acetone); mp 123–125°C; UV nm (log ϵ) 260 (4.3), 260 (4.52); IR 3426, 1738 and 1651 cm^{-1}; HRMS calc. for $C_{33}H_{44}O_6$ 536.3141, found 536.3137; m/z 536 (M$^+$), 270 (65%), 98 (100%).

Genistein-4′-monostearate 7. 77%; white solid (acetone); mp 115–117°C; UV nm (log ϵ) 262 (4.4); IR 3361, 1747 and 1659 cm^{-1}; HRMS calc. for $C_{33}H_{44}O_6$ 536.3141, found 536.3138; m/z 536 (M$^+$), 270 (70%), 98 (100%).

Genistein-7,4′-distearate 8. 96%; white solid (acetone); mp 89–91°C; UV nm (log ϵ) 257 (4.5); IR 1767, 1751 and 1648 cm^{-1}; HRMS calc. 802.5742 for $C_{51}H_{78}O_7$, found 802.5890; m/z 802 (M$^+$), 536 (40%), 270 (100%).

Daidzein-7-monooleate 9. 81%; white solid (acetone–methanol); mp 104–106°C; IR 3422, 1760 and 1642 cm^{-1}; UV nm (logϵ) 259 (4.5); HRMS calc. for $C_{33}H_{42}O_5$ 518.3042, found 518.3032; m/z 518 (M$^+$), 254 (100%).

Daidzein-4′-monooleate 10. 79%; white semi-solid; UV nm (log ϵ) 250 (4.7), 300 (4.3); IR 3319, 1739 and 1645 cm^{-1}; HRMS calc. for $C_{33}H_{42}O_5$ 518.3042, found 518.3044; m/z 518 (M$^+$), 254 (100%).

Daidzein-7,4′-dioleate 11. White semi-solid; UV nm (log ϵ) 250 (4.4), 305 (3.9); IR 1749 (broad) and 1644 cm^{-1}; HRMS calc. for $C_{51}H_{74}O_6$ 782.5485, found 782.5469; m/z 782 (M$^+$), 518 (10%), 254 (100%).

Genistein-7-monooleate 12. 87%; white solid (acetone–methanol); mp 80–82°C; UV nm (log ϵ) 260 (4.5); IR 3420, 1762 and 1648 cm^{-1}; HRMS calc. for $C_{33}H_{42}O_6$ 534.3000, found 534.2981; m/z 534 (M$^+$), 270 (100%).

Genistein-4′-monooleate 13. 80%; white semi-solid; UV nm (log ϵ) 261 (4.7); IR 3395, 1750 and 1651 cm^{-1}; HRMS calc. for $C_{33}H_{42}O_6$ 534.3000, found 534.2982; m/z 534 (M$^+$), 270 (100%).

Genistein-7,4′-dioleate 14. 95%; white semi-solid; UV nm (log ϵ) 254 (4.4); IR 1764 and 1644 cm^{-1}; HRMS calc. 798.54291 for $C_{51}H_{74}O_7$, found 798.5535; m/z (range 400–800 m/z) 798 (M$^+$), 534 (100%).

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