Sesquiterpenoid Derivatives from *Ferula ferulioides*. V[1)]

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Nine novel prenyl-dihydrofurocoumarin-type sesquiterpenoid derivatives, 2,3-dihydro-7-hydroxy-2*R,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin, 2,3-dihydro-7-hydroxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadien-6-onyl]-furo[3,2-*c*]coumarin, 2,3-dihydro-7-hydroxy-2*S**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin, 2,3-dihydro-7-hydroxy-2*R**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin, 2,3-dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin, 2,3-dihydro-7-methoxy-2*R**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin, 2,3-dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadien-6-onyl]-furo[3,2-*c*]coumarin, and 2,3-dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin, were isolated from the roots of *Ferula ferulioides*. The structures were established by comprehensive spectral analysis. The biosynthetic pathway leading to these prenyl-furocoumarin-type sesquiterpenoids is proposed based on their structures.**

Key words *Ferula ferulioides*; Umbelliferae; sesquiterpenoid; prenyl-dihydrofurocoumarin

Ferula ferulioides (STEUD.) KOROVIN (Umbelliferae) grows in Bulgan Somon of Hovd City, Mongolia, and has been used as a traditional medicine. In previous papers[1)] in this series,[2—4)] we reported the isolation of prenyl-furocoumarin-type sesquiterpenoid derivatives (**1**—**4**) from *F. ferulioides*. Those coumarins are 3-prenyl-furocoumarin-type sesquiterpenoid derivatives, in which the prenyl side chain is attached to the C-3 position of the furocoumarin moiety.

The present paper deals with the isolation and structural elucidation of nine novel 2-prenyl-dihydrofurocoumarin-type sesquiterpenoid derivatives, in which the prenyl side chain is attached to the C-2 position of the furocoumarin moiety. The 2-prenyl-dihydrofurocoumarin-type compounds were isolated from *F. communis* and Brachyclados *megalanthus*.[5)] Fercoprolone, which is isolated from *F. communis*,[5a)] was reported to be the major toxin of this plant, and total synthesis of fercoprolone was reported.[6)]

The dried and powdered roots were extracted with methanol, and removal of the solvent gave a waxy solid that was extracted with ethyl acetate and water. From the ethyl acetate extract, nine novel prenyl-dihydrofurocoumarin-type sesquiterpenoids (**5**—**13**) were isolated and identified.

The molecular formula of compound **5** was determined to be $C_{24}H_{30}O_4$ ($[M]^+$ at *m/z* 382.2142) by high-resolution mass spectrometry (HR-MS). The ^{1}H-NMR and ^{13}C-NMR spectra of **5** showed the existence of a 1,2,4-trisubstituted benzene ring (δ_H 6.85, 7.18, 7.53), three olefinic-methyl groups (δ_H 1.58, 1.58, 1.67; δ_C 16.0, 17.7, 25.7), two trisubstituted double bonds (δ_H 5.06, 5.10), an ester (δ_C 162.4), and two quaternary carbon signals at δ_C 103.2, 166.1 assigned to C-3a and C-9b. In addition, the characteristic absorption of the carbonyl group (ν 1699 cm^{-1}) in the IR spectrum of **5** supported the presence of a conjugated δ-lactone structure in this compound. These spectral data were similar to those of 4-oxgenated-3-prenyl coumarin derivatives.[7—9)] This structure was common to compounds **1**—**4**.

The NMR signals assigned to a methine (δ_H 3.30, q, J=7 Hz; δ_C 41.9) attached to a secondary methyl group (δ_H 1.31, d, J=7 Hz; δ_C 14.1) and to a tertiary methyl group (δ_H 1.46; δ_C 20.5) at C-2 revealed the presence of a dimethyldihydrofuran moiety.

We confirmed the location of the coumarin, furan, and prenyl side chain units based on a heteronuclear multiple-bond correlation (HMBC) spectrum. The structure of the side chain was deduced from a nuclear Overhauser and exchange spectroscopy (NOESY) experiment, in which cross-peaks were observed from the H-3′/H-5′ and H-7′/H-9′ pairs. This indicated an *E* configuration for the C-3′–C-4′ double bond. Thus, compound **5** was identified to be 2,3-dihydro-7-hydroxy-2,3-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin.

Compound **5**, like compounds **1**—**4**, is presumably a racemate at the chiral centers C-2 and C-3, because it showed an optical rotation of ±0° ($[\alpha]_D^{22}$). Compound **6** had an $[M]^+$ peak at *m/z* 382.2143 ($C_{24}H_{30}O_4$). Although the ^{1}H- and ^{13}C-NMR spectra of **6** were slightly different from those of **5**, especially at C-3 (**5**: δ_C 41.9, **6**: δ_C 44.3), C-1′ (**5**: δ_C 41.7, **6**: δ_C 35.2), and $Me_{C\text{-}2}$ (**5**: δ_C 20.5, **6**: δ_C 25.4). The HMBC experiment suggested that the planar structure of **6** was the same as that of **5**. Therefore, **6** may be a diastereomer of **5** at chiral centers C-2 and C-3. A series of NOESY experiments was carried out with **5** and **6** to identify the relative stereochemistry of the dimethyldihydrofuran moiety at C-2 and C-3. Cross-peaks between H-3/H-$Me_{C\text{-}2}$ were observed in **6**, but not in **5**, while those between H-3/H-1′, H-3/H-2′, and H-$Me_{C\text{-}2}$/H-$Me_{C\text{-}3}$ appeared in **5**. These NOE results indicated that the relation between the $Me_{C\text{-}2}$ and $Me_{C\text{-}3}$ is *cis* in **5** and *trans* in **6**. Thus, compounds **5** and **6** were identified to be 2,3-dihydro-7-hydroxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin and 2,3-dihydro-7-hydroxy-2*R**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin, respectively.

Compound **7** showed an $[M]^+$ peak at *m/z* 396.1937 ($C_{24}H_{28}O_5$). The ^{1}H- and ^{13}C-NMR spectra of **7** were similar to those of **5**, except for the presence of one more carbonyl signal (δ_C 199.5) assigned to C-6′. Compound **7** is thus 2,3-

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Table 1. ^{1}H-NMR Spectral Data of Compounds **5**—**13** in $CDCl_3$ (500 MHz)

	5	**6**	**7**	**8**	**9**
3	3.30 (1H, q, *J*=7 Hz)	3.20 (1H, q, *J*=7 Hz)	3.27 (1H, q, *J*=7 Hz)	3.28 (1H, q, *J*=7 Hz)	3.21 (1H, q, *J*=7 Hz)
6	7.18 (1H, d, *J*=2 Hz)	7.08 (1H, brs)	6.98 (1H, d, *J*=2 Hz)	7.06[a)]	7.05 (1H, d, *J*=2 Hz)
8	6.85 (1H, dd, *J*=2, 9 Hz)	6.82 (1H, brd, *J*=9 Hz)	6.82 (1H, dd, *J*=2, 9 Hz)	6.82 (1H, dd, *J*=2, 9 Hz)	6.82 (1H, dd, *J*=2, 9 Hz)
9	7.53 (1H, d, *J*=9 Hz)	7.54 (1H, d, *J*=9 Hz)	7.51 (1H, d, *J*=9 Hz)	7.52 (1H, d, *J*=9 Hz)	7.53 (1H, d, *J*=9 Hz)
1′	1.81 (2H, m)	1.89 (2H, m)	1.85 (2H, m)	1.82 (2H, m)	1.87 (2H, m)
2′	2.11 (2H, m)	2.23 (2H, m)	2.17 (2H, m)	2.15 (2H, m)	2.13 (2H, m)
3′	5.10 (1H, t, *J*=7 Hz)	5.16 (1H, t, *J*=7 Hz)	5.23 (1H, brt)	5.19 (1H, t, *J*=7 Hz)	5.27 (1H, brt)
5′	1.95 (2H, m)	1.99 (2H, m)	3.02 (1H, brs) 3.08 (1H, brs)	3.19 (2H, s)	3.25 (2H, s)
6′	2.03 (2H, m)	2.08 (2H, m)			
7′	5.06 (1H, t, *J*=7 Hz)	5.08 (1H, t, *J*=7 Hz)	6.12 (1H, s)	5.85 (1H, s)	5.89 (1H, s)
9′	1.67 (3H, s)	1.68 (3H, s)	1.87 (3H, s)	7.06[a)]	7.07 (1H, s)
2Me	1.46 (3H, s)	1.48 (3H, s)	1.45 (3H, s)	1.45 (3H, s)	1.48 (3H, s)
3Me	1.31 (3H, d, *J*=7 Hz)	1.29 (3H, d, *J*=7 Hz)	1.31 (3H, d, *J*=7 Hz)	1.30 (3H, d, *J*=7 Hz)	1.29 (3H, d, *J*=7 Hz)
4′Me	1.58 (3H, s)	1.64 (3H, s)	1.60 (3H, s)	1.58 (3H, s)	1.64 (3H, s)
8′Me	1.58 (3H, s)	1.60 (3H, s)	2.14 (3H, s)	1.97 (3H, s)	1.98 (3H, s)

	10	**11**	**12**	**13**
3	3.29 (1H, q, *J*=7 Hz)	3.19 (1H, q, *J*=7 Hz)	3.28 (1H, q, *J*=7 Hz)	3.28 (1H, q, *J*=7 Hz)
6	6.84 (1H, d, *J*=2 Hz)	6.85 (1H, brs)	6.85 (1H, brs)	6.84 (1H, brs)
8	6.83 (1H, dd, *J*=2, 8.5 Hz)	6.84 (1H, dd, *J*=2, 9 Hz)	6.84 (1H, dd, *J*=2, 9 Hz)	6.82 (1H, dd, *J*=2, 9 Hz)
9	7.53 (1H, d, *J*=8.5 Hz)	7.54 (1H, d, *J*=9 Hz)	7.53 (1H, d, *J*=9 Hz)	7.52 (1H, d, *J*=9 Hz)
1′	1.80 (2H, m)	1.89 (2H, m)	1.85 (2H, m)	1.82 (2H, m)
2′	2.12 (2H, m)	2.19 (2H, m)	2.18 (2H, m)	2.15 (2H, m)
3′	5.09 (1H, t, *J*=7 Hz)	5.17 (1H, t, *J*=7 Hz)	5.23 (1H, brt)	5.20 (1H, t, *J*=7 Hz)
5′	1.95 (2H, m)	2.00 (2H, m)	3.02 (2H, s)	3.19 (2H, s)
6′	2.03 (2H, m)	2.07 (2H, m)		
7′	5.07 (1H, t, *J*=7 Hz)	5.09 (1H, t, *J*=7 Hz)	6.08 (1H, s)	5.85 (1H, s)
9′	1.67 (3H, s)	1.68 (3H, s)	1.87 (3H, s)	7.05 (1H, s)
2Me	1.45 (3H, s)	1.48 (3H, s)	1.45 (3H, s)	1.45 (3H, s)
3Me	1.31 (3H, d, *J*=7 Hz)	1.29 (3H, d, *J*=7 Hz)	1.31 (3H, d, *J*=7 Hz)	1.30 (3H, d, *J*=7 Hz)
4′Me	1.58 (3H, s)	1.64 (3H, s)	1.61 (3H, s)	1.58 (3H, s)
8′Me	1.58 (3H, s)	1.60 (3H, s)	2.13 (3H, s)	1.97 (3H, s)
OMe	3.87 (3H, s)	3.87 (3H, s)	3.87 (3H, s)	3.87 (3H, s)

a) Overlapped with other signals.

dihydro-7-hydroxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadien-6-onyl]-furo[3,2-*c*]coumarin.

Compound **8** had an $[M]^+$ peak at *m/z* 394.1780 ($C_{24}H_{26}O_5$). The ^{1}H- and ^{13}C-NMR spectra of **8** were similar to those of **5**, except for the presence of a 4-methyl-2-furyl system (δ_H 1.97, 5.85, 7.06; δ_C 9.80, 108.9, 120.5, 137.8, 154.0) at C-5′ in place of the trisubstituted olefin present in **5**. Compound **9** had an $[M]^+$ peak at *m/z* 394.1774 ($C_{24}H_{26}O_5$). The ^{1}H- and ^{13}C-NMR spectra of **9** were slightly different from those of **8**, especially at C-3 (**8**: δ_C 42.0, **9**: δ_C 44.3), C-1′ (**8**: δ_C 41.5, **9**: δ_C 35.0), and $Me_{C\text{-}2}$ (**8**: δ_C 20.4, **9**: δ_C 25.4), but these signals were similar to those of **6**. The HMBC experiment suggested that **9** may be a diastereomer of **8** at chiral centers C-2 and C-3. A series of NOESY experiments was carried out with **8** and **9**, and cross-peaks were observed from the pair H-3/H-$Me_{C\text{-}2}$ in **9**, but not in **8**. These NOE results together with the chemical shifts of the carbon signals indicated that the stereochemistry of **8** and **9** is same as that of **5** and **6**. Thus, compounds **8** and **9** were assigned to be 2,3-dihydro-7-hydroxy-2*S**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin and 2,3-dihydro-7-hydroxy-2*R**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin, respectively.

Compounds **10** and **11** had an $[M]^+$ peak at *m/z* 396.2301

Table 2. ^{13}C-NMR Spectral Data of Compounds **5**—**13** in $CDCl_3$ (125 MHz)

	5	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
2	97.2	96.5	96.8	97.0	96.4	96.8	96.3	96.7	96.7
3	41.9	44.3	42.0	42.0	44.3	42.0	44.4	42.1	42.1
3a	103.2	103.7	103.6	103.4	103.7	103.6	104.0	103.6	103.6
4	162.4	162.0	161.9	162.0	162.0	161.3	161.3	161.3	161.2
5a	156.7	156.7	156.7	156.7	156.7	156.9	156.9	156.9	156.9
6	103.3	103.2	103.3	103.3	103.3	100.7	100.7	100.7	100.7
7	160.8	160.3	160.5	160.3	160.3	163.2	163.2	163.2	163.2
8	113.4	113.0	113.1	113.1	113.0	112.2	112.2	112.3	112.2
9	124.2	124.2	124.2	124.2	124.2	123.8	123.8	123.8	123.8
9a	105.8	106.2	106.1	106.1	106.2	106.3	106.4	106.2	106.3
9b	166.1	165.1	165.7	165.7	165.5	165.1	165.0	165.1	165.1
1′	41.7	35.5	41.4	41.5	35.0	41.8	35.2	41.5	41.4
2′	22.1	22.7	22.4	22.3	22.9	22.1	22.8	22.4	22.3
3′	123.1	123.5	128.1	125.4	125.8	123.2	123.6	128.0	125.4
4′	136.0	135.9	130.5	132.9	132.7	136.0	135.9	130.6	132.8
5′	39.6	39.6	55.1	38.4	38.4	39.6	39.7	55.1	38.4
6′	26.6	26.6	199.5	154.0	154.0	26.6	26.7	199.1	154.0
7′	124.2	124.2	122.9	108.9	109.0	124.2	124.2	122.9	108.9
8′	131.5	131.5	156.7	120.5	120.6	131.4	131.5	156.1	120.5
9′	25.7	25.7	27.8	137.8	137.8	25.7	25.7	27.7	137.8
2Me	20.5	25.4	20.5	20.4	25.4	20.5	25.4	20.5	20.5
3Me	14.1	13.5	14.1	14.1	13.6	14.1	13.5	14.1	14.1
4′Me	16.0	16.0	16.5	15.9	16.0	16.0	16.0	16.5	15.9
8′Me	17.7	17.7	20.8	9.8	9.8	17.7	17.7	20.7	9.8
OMe						55.7	55.7	55.8	55.7

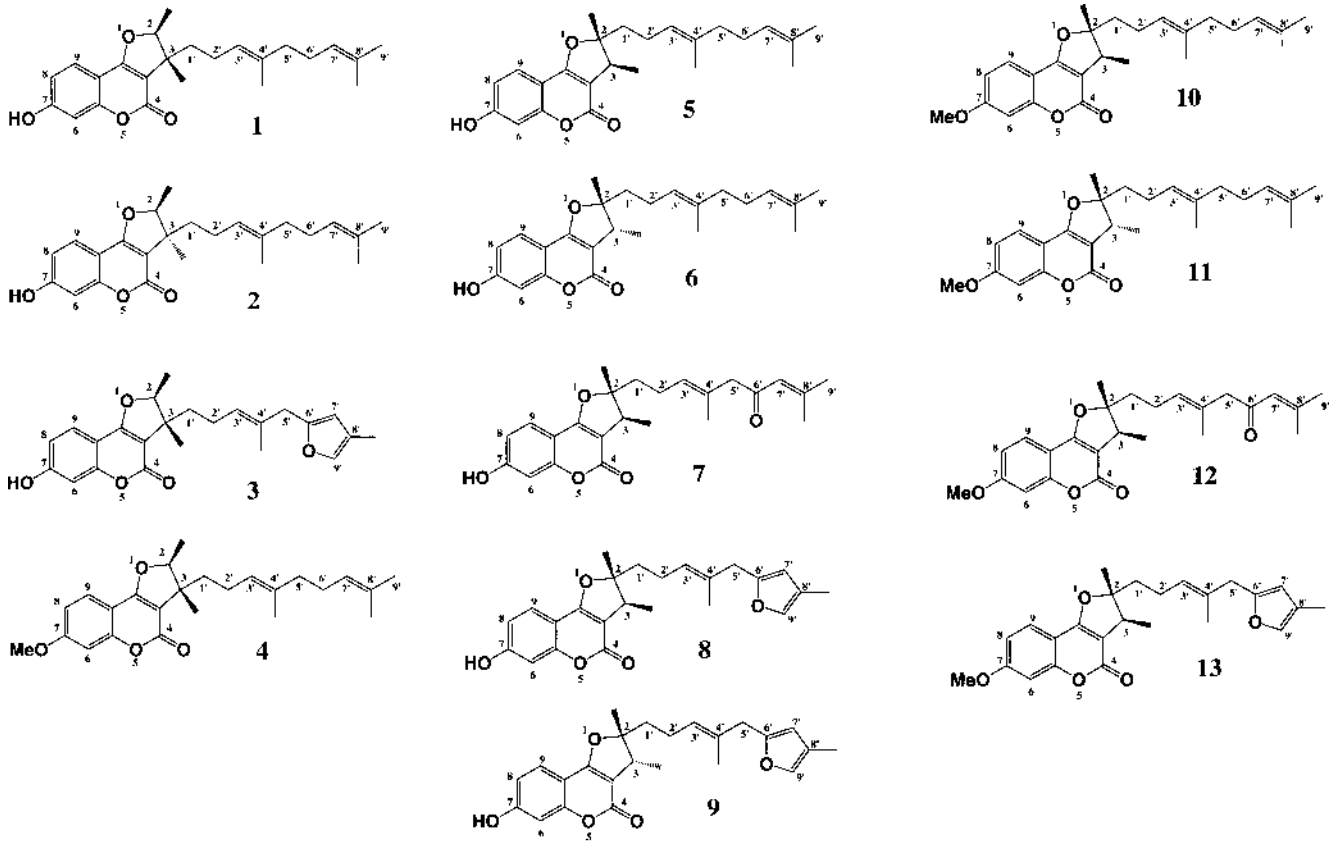

Fig. 1. Structures of Compounds **5**—**13**

($C_{25}H_{32}O_4$) and *m/z* 396.2296 ($C_{25}H_{32}O_4$), respectively. The ^{1}H- and ^{13}C-NMR spectra of **10** and **11** were similar to those of **5** and **6**, except for the presence of a methoxy group (δ_H 3.87; δ_C 55.7) at C-7. The chemical shifts of the signals of C-3, C-1′, and $Me_{C\text{-}2}$ and a series of NOESY experiments with **10** and **11** indicate that their stereochemistry is the same as that of **5** and **6**. Thus, compounds **10** and **11** were assigned to be 2,3-dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin and 2,3-dihydro-7-methoxy-2*R**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin, respectively.

Compound **12** showed an $[M]^+$ peak at *m/z* 410.2086 ($C_{25}H_{30}O_5$). NMR spectra show that **12** has a methoxy compound at C-7 of **7**. Compound **12** is thus 2,3-dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadien-6-onyl]-furo[3,2-*c*]coumarin. Compound **13** showed an $[M]^+$ peak at *m/z* 408.1936 ($C_{25}H_{28}O_5$). NMR spectra show that **13** has a methoxy compound at C-7 of **8**. Compound **13** is thus 2,3-dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin.

The chemical shifts of the ^{1}H- and ^{13}C-NMR spectra were very similar among compounds **5**, **7**, **8**, **10**, **12**, and **13**, indicating that they have same relative stereochemistry, the *cis*-relation between $Me_{C\text{-}2}$ and $Me_{C\text{-}3}$. In contrast, the chemical shifts of these compounds were slightly different from those of **6**, **9**, and **11** which have the *trans*-relation between $Me_{C\text{-}2}$ and $Me_{C\text{-}3}$. Compounds **5**—**13** were racemic compounds, since they were optically inactive.

In a previous paper, we proposed a biosynthetic pathway leading to the sesquiterpenoid compounds **1**—**4** isolated from *F. ferulioides*.[1] Isolation of compounds **5**—**13** described in this paper suggests the presence of an additional biosynthetic route branched from the hypothetical precursor C as described in Fig. 2.

The hydroxylation of the vinyl group of the intermediate C through hydration leads to the formation of the hypothetical intermediate D, which is then converted to the third hypothetical intermediate F by intramolecular esterification. Furthermore, the dehydration of F leads to compounds **1**—**4**. On the other hand, the rearrangement of the C6–C3 moiety of the intermediate C to the C-2 position of the farnesyl moiety may lead to the formation of a hypothetical intermediate E, which is then converted to the hypothetical intermediate G by intramolecular esterification. Furthermore, the dehydration of G leads to compounds **5**—**13**. It will be interesting to examine the pharmacological activities of the sesquiterpenoid derivatives isolated from *F. ferulioides*.

Experimental

General Procedures NMR spectra were recorded on a JEOL JNM-A500 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Electron-impact mass spectra (EI-MS) were recorded on a JEOL JMS-DX300 spectrometer. Optical rotation was measured with a JASCO DIP-4 digital polarimeter. IR spectra were recorded on a Shimadzu FTIR-8100 spectrometer.

Plant Material The roots of *F. ferulioides* (Steud.) Korovin were collected in July 1996 at Bulgan Somon of Hovd City. Voucher specimens have been deposited in the Botanical Department of Mongolian State University.

Extraction and Isolation The dried and pulverized roots of *F. ferulioides* (400 g) were extracted successively with methanol under reflux. After evaporation of the solvent, part of the methanol extract (40 g) was partitioned between ethyl acetate and water. The ethyl acetate layer was evapo-

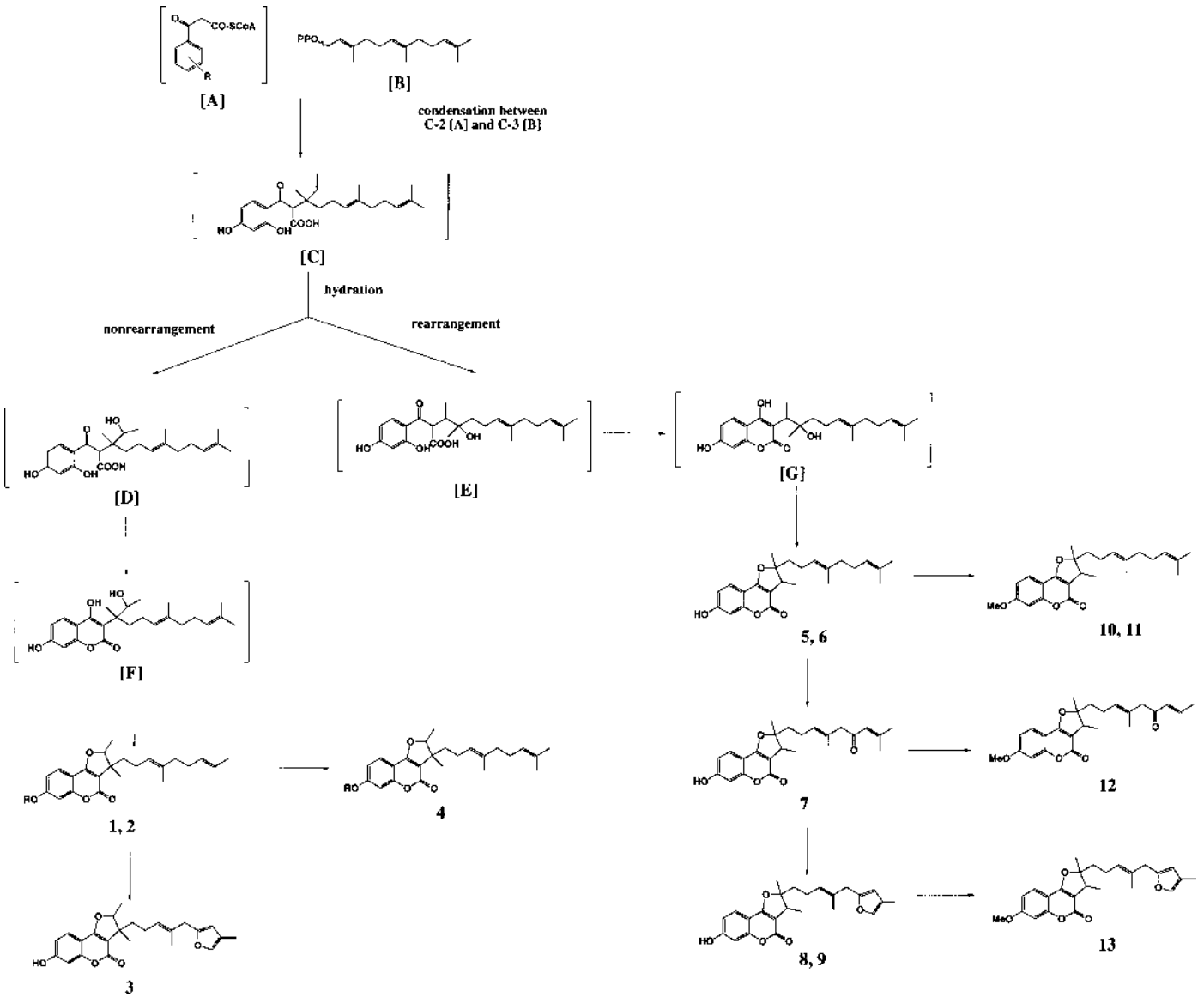

Fig. 2. Proposed Biosynthetic Pathway to Compounds **5**—**13**

rated under reduced pressure. The residue was chromatographed on silica gel with hexane–ethyl acetate (10 : 1—1 : 1) to afford 12 fractions. Fraction 4 was subjected to RP-18 Lober chromatography (80% CH_3CN) to give **10** (5 mg), **11** (5 mg), and **13** (7 mg); fraction 6 was subjected to RP-18 Lober chromatography (45—65% CH_3CN) to give **5** (7 mg) and **12** (4 mg); fraction 7 was subjected to RP-18 Lober chromatography (65% CH_3CN) to give **6** (2 mg); fraction 8 was subjected to silica gel chromatography with hexane–ethyl acetate (10 : 1—1 : 1) to give **8** (5 mg) and **9** (3 mg); and fraction 11 was subjected to RP-18 Lober chromatography (55—60% CH_3CN) to give **7** (4 mg).

2,3-Dihydro-7-hydroxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin (**5**): Oil, $[\alpha]_D^{23}=\pm 0°$ (c=0.6, $CHCl_3$), EI-MS *m/z*: 382 $[M]^+$, 231 $[C_{13}H_{11}O_4]^+$, HR-MS *m/z*: 382.2142 $[M]^+$ (Calcd for $C_{24}H_{30}O_4$: 382.2144), IR ν_{max} ($CHCl_3$): 1699 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

2,3-Dihydro-7-hydroxy-2*R**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin (**6**): Oil, $[\alpha]_D^{22}=\pm 0°$ (c=0.8, $CHCl_3$), EI-MS *m/z*: 382 $[M]^+$, 231 $[C_{13}H_{11}O_4]^+$, HR-MS *m/z*: 382.2143 $[M]^+$ (Calcd for $C_{24}H_{30}O_4$: 382.2144), IR ν_{max} ($CHCl_3$): 1700 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

2,3-Dihydro-7-hydroxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadien-6-onyl]-furo[3,2-*c*]coumarin (**7**): Oil, $[\alpha]_D^{21}=\pm 0°$ (c=0.7, $CHCl_3$), EI-MS *m/z*: 396 $[M]^+$, 231 $[C_{13}H_{11}O_4]^+$, HR-MS *m/z*: 396.1937 $[M]^+$ (Calcd for $C_{24}H_{28}O_5$: 396.1937), IR ν_{max} ($CHCl_3$): 1707 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

2,3-Dihydro-7-hydroxy-2*S**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin (**8**): Oil, $[\alpha]_D^{23}=\pm 0°$ (c=0.6, $CHCl_3$), EI-MS *m/z*: 394 $[M]^+$, 231 $[C_{13}H_{11}O_4]^+$, HR-MS *m/z*: 394.1780 $[M]^+$ (Calcd for $C_{24}H_{26}O_5$: 394.1780), IR ν_{max} ($CHCl_3$): 1705 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

2,3-Dihydro-7-hydroxy-2*R**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin (**9**): Oil, $[\alpha]_D^{23}=\pm 0°$ (c=0.7, $CHCl_3$), EI-MS *m/z*: 394 $[M]^+$, 231 $[C_{13}H_{11}O_4]^+$, HR-MS *m/z*: 394.1774 $[M]^+$ (Calcd for $C_{24}H_{26}O_5$: 394.1780), IR ν_{max} ($CHCl_3$): 1705 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

2,3-Dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin (**10**): Oil, $[\alpha]_D^{24}=\pm 0°$ (c=0.5, $CHCl_3$), EI-MS *m/z*: 396 $[M]^+$, 245 $[C_{14}H_{13}O_4]^+$, HR-MS *m/z*: 396.2301 $[M]^+$ (Calcd for $C_{25}H_{32}O_4$: 396.2300), IR ν_{max} ($CHCl_3$): 1707 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

2,3-Dihydro-7-methoxy-2*R**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadienyl]-furo[3,2-*c*]coumarin (**11**): Oil, $[\alpha]_D^{24}=\pm 0°$ (c=0.4, $CHCl_3$), EI-MS *m/z*: 396 $[M]^+$, 245 $[C_{14}H_{13}O_4]^+$, HR-MS *m/z*: 396.2296 $[M]^+$ (Calcd for $C_{25}H_{32}O_4$: 396.2300), IR ν_{max} ($CHCl_3$): 1707 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

2,3-Dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4,8-dimethyl-3(*E*),7-nonadien-6-onyl]-furo[3,2-*c*]coumarin (**12**): Oil, $[\alpha]_D^{23}=\pm 0°$ (c=0.7, $CHCl_3$), EI-MS *m/z*: 410 $[M]^+$, 245 $[C_{14}H_{13}O_4]^+$, HR-MS *m/z*: 410.2086 $[M]^+$ (Calcd

for $C_{25}H_{30}O_5$: 410.2093), IR ν_{max} ($CHCl_3$): 1707 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

2,3-Dihydro-7-methoxy-2*S**,3*R**-dimethyl-2-[4-methyl-5-(4-methyl-2-furyl)-3(*E*)-pentenyl]-furo[3,2-*c*]coumarin (**13**): Oil, $[\alpha]_D^{23} = \pm 0°$ (c=0.6, $CHCl_3$), EI-MS *m*/*z*: 408 $[M]^+$, 245 $[C_{14}H_{13}O_4]^+$, HR-MS *m*/*z*: 408.1936 $[M]^+$ (Calcd for $C_{25}H_{28}O_5$: 408.1937), IR ν_{max} ($CHCl_3$): 1707 cm^{-1}. ^{1}H-NMR: see Table 1. ^{13}C-NMR: see Table 2.

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