Glycinoprenols: Novel Polyprenols Possessing a Phytyl Residue from the Leaves of Soybean

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Three novel polyprenols, named glycinoprenol-9, -10, and -11, in addition to ficaprenols were isolated from the leaves of soybean, *Glycine max* Merrill. The glycinoprenols were found to possess a phytyl residue, four to six internal (*Z*)-prenyl residues, and a *Z* α-terminal residue aligned in that order on the basis of their IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data. The configurations of two chiral centers in the phytyl residue were determined to be all *R* by a combination of chemical and spectroscopic methods.

Polyprenols comprising (*E*)- and (*Z*)-prenyl residues can be classified into three groups, betulaprenol-type polyprenols, ficaprenol-type polyprenols, and polyprenols having one or more saturated prenyl residues. Betulaprenol-type polyprenols have a farnesyl residue at the ω-end of their prenyl chain and have been found in the woody tissue of *Betula verrucosa*,[1] the cells of the bacterium *Lactobacillus plantarum*,[2] and the needles and leaves of gymnosperms.[3-5] Ficaprenol-type polyprenols from the leaves of angiosperms[6-10] have a geranylgeranyl residue at the ω-end of their prenyl chain. Some polyprenols contain one or more saturated prenyl residues at the α-terminal residue and/or the ω-end of their prenyl chain. Dolichols characterized by a saturated α-terminal residue have been found in animals,[11] plants,[12] and microorganisms.[13,14] Hexahydropolyprenols, isolated from *Aspergillus fumigatus*, have two saturated prenyl residues at the ω-end of their prenyl chain.[15] Another shorter member of the isoprenoid alcohols, C_{25}-prenol, comprises a phytyl residue and a *Z* α-terminal residue, and it was isolated from the leaves of *Solanum tuberosum*.[16]

We have recently discovered an unusual hydrogen elimination during the elongation of the (*Z*)-prenyl chain in the biosynthesis of ficaprenol-type polyprenols, malloprenols, in the leaves of *Mallotus japonicus*.[17] The unusual hydrogen elimination was contrary to Cornforth's basic picture for the stereochemistry of prenylation in the biosynthesis of isoprenoids.[18-21] Such an elimination of the reversed hydrogen has been established to be common to the ficaprenol-type polyprenols in higher plants.[9,10] In the course of studies on the stereochemistry during the biosynthesis of polyprenols, we investigated chemical constituents in the leaves of soybean (*Glycine max* Merrill) and isolated the two series of homologues of polyprenols: one series contained highly saturated polyprenols, named glycinoprenol-9, -10, and -11, and another contained ficaprenols. We here describe the evidence that led to establishment of the structures of novel polyprenols, glycinoprenol-9, -10, and -11.

Results and Discussion

A hexane-soluble fraction of the leaves of soybean was subjected to silica gel column chromatography to give a polyprenol fraction. The reversed-phase HPLC of the polyprenol fraction showed six peaks due to polyprenols, as shown in Figure 1. The polyprenol fraction was repeatedly purified by reversed-phase HPLC to give compounds **1**–**6**, which are numbered in the order of increasing retention time on reversed-phase HPLC. The proportions of compounds **1**–**6** were 19, 1, 70, 7, 2, and 1%, respectively. Compounds **1**, **3**, and **5** were found to be ficaprenol-10, -11, and -12, respectively, by direct comparison with authentic samples on reversed-phase HPLC. The identities were supported by their IR, ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectral data. Compounds **2**, **4**, and **6** were named glycinoprenol-9, -10, and -11, respectively.

Glycinoprenol-10 (**4**) has a molecular formula of $C_{50}H_{88}O$ on the basis of the appearance of a molecular ion peak at *m/z* 704.6833 ($[C_{50}H_{88}O]^+$) and a dehydrated ion peak at *m/z* 686.6699 ($[C_{50}H_{86}]^+$) in the high-resolution EI-MS. The ^{1}H NMR spectrum of **4** indicated the presence of olefinic protons [δ 5.44 (1 H, dt, *J* = 7.2 and 1.3 Hz) and 5.08–5.15 (6 H, m)] and a hydroxylated methylene [δ 4.09 (2 H, dd, *J* = 7.2 and 0.9 Hz)]. Decoupling experiments showed the presence of the hydroxylated methylene protons in the neighborhood of one (δ 5.44) of the olefinic protons. The methyl proton signals at δ 0.84 (6 H, d, *J* = 6.6 Hz) and 0.86 (6 H, d, *J* = 6.7 Hz) suggested the presence of saturated prenyl residues. The methyl proton signal at δ 1.59 (3 H, br s) indicated the presence of one

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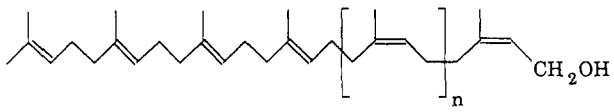
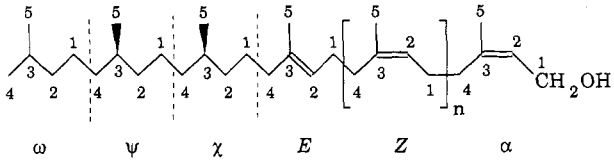
(1) Wellburn, A. R.; Hemming, F. W. *Nature (London)* **1966**, *212*, 1364–1366.
(2) Gough, D. P.; Kirby, A. L.; Richards, J. B.; Hemming, F. W. *Biochem. J.* **1970**, *118*, 167–170.
(3) Ibata, K.; Mizuno, M.; Takigawa, T.; Tanaka, Y. *Biochem. J.* **1983**, *213*, 305–311.
(4) Ibata, K.; Mizuno, M.; Tanaka, Y.; Kageyu, A. *Phytochemistry* **1984**, *23*, 783–786.
(5) Ibata, K.; Kageyu, A.; Takigawa, T.; Okada, M.; Nishida, T.; Mizuno, M.; Tanaka, Y. *Phytochemistry* **1984**, *23*, 2517–2521.
(6) Stone, K. J.; Wellburn, A. R.; Hemming, F. W.; Pennock, J. F. *Biochem. J.* **1967**, *102*, 325–330.
(7) Suga, T.; Shishibori, T. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2098–2104.
(8) Suga, T.; Shishibori, T.; Nakaya, K. *Phytochemistry* **1980**, *19*, 2327–2330.
(9) Suga, T.; Aoki, T.; Hirata, T.; Saragai, Y. *Chem. Lett.* **1983**, 1467–1470.
(10) Suga, T; Hirata, T.; Aoki, T.; Kataoka, T. *J. Am. Chem. Soc.* **1986**, *108*, 2366–2371.
(11) Burgos, J.; Hemming, F. W.; Pennock, J. F.; Morton, R. A. *Biochem. J.* **1963**, *88*, 470–482.
(12) Brett, C. T.; Leloir, L. F. *Biochem. J.* **1977**, *161*, 93–101.
(13) Richards, J. B.; Hemming, F. W. *Biochem. J.* **1972**, *128*, 1345–1352.
(14) Jung, P.; Tanner, W. *Eur. J. Biochem.* **1973**, *37*, 1–6.
(15) Stone, K. J.; Butterworth, P. H. W.; Hemming, F. W. *Biochem. J.* **1967**, *102*, 443–455.
(16) Toyoda, M.; Asahina, M.; Fukawa, H.; Shimizu, T. *Tetrahedron Lett.* **1969**, 4879–4882.
(17) Suga, T.; Hirata, T.; Aoki, T.; Shishibori, T. *J. Am. Chem. Soc.* **1983**, *105*, 6178–6179.
(18) Cornforth, J. W.; Cornforth, R. H.; Donninger, C.; Popjak, G. *Proc. R. Soc. London, B* **1966**, *163*, 492–514.
(19) Goodwin, T. W.; Williams, R. J. H. *Proc. R. Soc. London, B* **1966**, *163*, 515–518.
(20) Popjak, G.; Cornforth, J. W. *Biochem. J.* **1966**, *101*, 553–568.
(21) Archer, B. L.; Barnard, D.; Cookbain, E. G.; Cornforth, J. W.; Cornforth, R. H.; Popjak, G. *Proc. R. Soc. London, B* **1966**, *163*, 519–523.

0022-3263/89/1954-3390$01.50/0

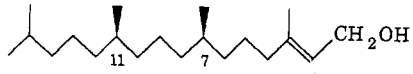


1 n = 5
3 n = 6
5 n = 7



2 n = 4
4 n = 5
6 n = 6

(*E*)-prenyl residue. The methyl proton signal at δ 1.74 (3 H, br d, J = 1.3 Hz) indicated that the α-terminal residue has the *Z* configuration.[3] The relative intensity of this signal to the methyl proton signals of internal (*Z*)-prenyl residues at δ 1.68 showed the presence of five internal (*Z*)-prenyl residues. Comparison of the ^{13}C NMR chemical shifts of **4** (Table I) with those of phytol (**7**),[22] lycopadiene,[23] and polyprenols isolated from *Ginkgo biloba*[3] indicated that a phytyl residue, five internal (*Z*)-prenyl residues, and a *Z* α-terminal residue are aligned in the order shown in the structure of **4**. This indication was supported by the fact that ozonolysis of **4** gave 6,10,14-trimethylpentadecan-2-one (**8**), levulinic acid, and oxalic acid. Therefore, glycinoprenol-10 (**4**) was characterized to be (2*Z*,6*Z*,10*Z*,14*Z*,18*Z*,22*Z*,26*E*)-3,7,11,15,19,23,27,31,35,39-decamethyl-2,6,10,14,18,22,26-tetracontaheptaen-1-ol.



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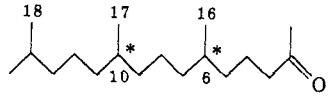

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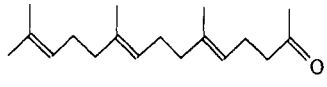

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Glycinoprenol-10 (**4**) has two chiral centers at C-31 and C-35. The absolute configuration of **4** was examined by a combination of the CD method, GLC analysis, and ^{13}C NMR spectroscopy as follows. First the configuration at C-31 of **4** was determined on the basis of the CD spectrum of the pentadecanone **8**. As shown in Figure 2, compound **8** showed a positive Cotton effect ($\Delta\epsilon_{284}$ = +0.020), which indicates its configuration at C-6 to be *R*.[24] As C-6 of compound **8** originates from C-31 of compound **4**, the configuration at C-31 of **4** is *R*. Next the relative config-

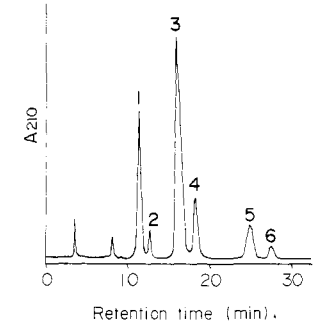

Figure 1. Reversed-phase HPLC of the polyprenol fraction from the leaves of soybean eluted with hexane–MeOH; flow rate, 1 mL/min.

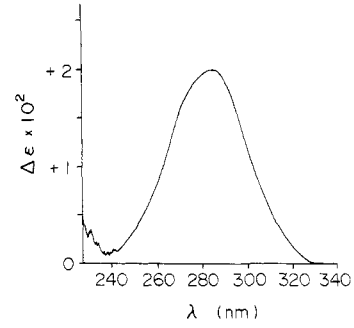

Figure 2. CD curve of **8** derived from **4** in hexane.

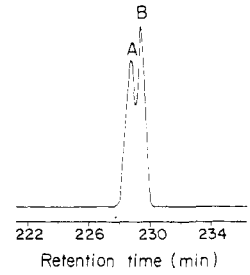

Figure 3. GLC of the racemic mixture of **8** derived from **9**: OV-1 glass-fused capillary column (0.2 mm × 50 m); column temperature, from 100 to 230 °C at 0.5 °C/min.

uration between C-31 and C-35 of **4** was examined by the GLC co-injection analysis of compound **8** with (6*R*,10*R*)-**8**[25] and a racemic mixture of **8** [(6*R*,10*R*)-, (6*S*,10*S*)-, (6*R*,10*S*)-, and (6*S*,10*R*)-**8**]. (6*R*,10*R*)-**8** was prepared from natural (7*R*,11*R*)-phytol (**7**) by ozonolysis. The racemic mixture of **8** was prepared from 6,10,14-trimethyl-5,9,13-pentadecatrien-2-one (**9**) by hydrogenation. The ratio of the mixture should be 1:1:1:1, if one assumes that it arose from **9** by stereorandom hydrogenation. The racemic mixture of **8** showed two peaks at retention time 228.6 min (peak A) and 229.3 min (peak B) on its GLC, as shown in Figure 3. The area ratio of peak A to peak B was approximately 1:1. The GC–mass spectra of the racemic mixture of **8** were recorded at 5-s intervals from the initial point (retention time 227.6 min) of peak A to the end point (retention time 230.1 min) of peak B. All the mass spectra were identical with each other and showed the mass patterns due to the planar structure of compound **8**. So the difference in the retention time between peaks A and B was considered to be due to a diastereomeric effect. The peak B was identical in retention time with the peak of (6*R*,10*R*)-**8** by the co-injection analysis of the racemic mixture of **8** with (6*R*,10*R*)-**8**. Accordingly, the peak B should be ascribed

(22) Gramatica, P.; Manitto, P.; Monti, D.; Speranza, G. *Tetrahedron* **1987**, *43*, 4481–4486.
(23) Metzger, P.; Casadevall, E. *Tetrahedron Lett.* **1987**, *28*, 3931–3934.
(24) Djerassi C.; Geller, L. E. *J. Am. Chem. Soc.* **1959**, *81*, 2789–2794.
(25) Burrell, J. W. K.; Garwood, R. F.; Jackman, L. M.; Oskay, E.; Weedon, B. C. L. *J. Chem. Soc. C* **1966**, 2144–2154.

Table I. ^{13}C NMR Chemical Shifts of 2, 4, and 6

position	2	4	6
3α	139.87	139.86	139.88
3E,3Z	136.07	136.06	136.07
	135.56	135.55	135.55
	135.40	135.38	135.38
	135.36	135.36	135.37
	135.29	135.27	135.27
		135.25	135.24 × 2
2Z,2α	124.99	125.02	125.02 × 2
	124.93	125.00	125.00
	124.89	124.94	124.94
	124.53	124.89	124.89
	124.48	124.53	124.52
		124.48	124.47
2E	123.90	123.91	123.91
1α	59.02	59.02	59.02
4E	40.05	40.05	40.04
2ω	39.38	39.38	39.38
2χ,2ψ	37.46	37.46	37.45
4χ,4ψ	37.42	37.42	37.42
	37.30	37.30	37.30
	36.71	36.71	36.71
3χ,3ψ	32.81	32.81	32.80
	32.72	32.72	32.72
4Z,4α	32.25	32.25	32.24
	32.22	32.23 × 2	32.22
	32.21	32.21	32.21 × 2
	32.19	32.19	32.20
	32.01	32.01	32.19
			32.01
3ω	27.98	27.98	27.98
1E	26.61	26.61	26.61
1Z	26.42	26.42	26.42
	26.41	26.41 × 2	26.41
	26.37	26.37	26.40
	26.32	26.32	26.39
			26.37
			26.32
1χ,1ψ	25.41	25.41	25.41
1ω	24.80	24.80	24.80
	24.49	24.49	24.48
5Z,5α	23.45 × 2	23.44 × 2	23.44 × 2
	23.44	23.43 × 3	23.43 × 3
	23.43	23.36	23.42
	23.36		23.36
4ω,5ω	22.71	22.71	22.71
	22.62	22.62	22.62
5χ,5ψ	19.75 × 2	19.75 × 2	19.75
			19.74
5E	15.88	15.87	15.87

to *syn*-8 [(6*R*,10*R*)- and (6*S*,10*S*)-8] and the peak A to *anti*-8 [(6*R*,10*S*)- and (6*S*,10*R*)-8]. The peak of compound 8 showed the same retention time as the peak B in the co-injection analysis with the racemic mixture of 8. Therefore, the relative configuration between C-6 and C-10 of compound 8 was assigned to be syn. This relative stereochemistry was supported by ^{13}C NMR spectroscopy. As given in Table II, (6*R*,10*R*)-8 showed two methyl signals assigned to 16-Me and 17-Me and the racemic mixture of 8 showed four methyl signals for these methyl groups. Since the differences in the chemical shifts between 19.52 and 19.58 and between 19.67 and 19.73 in the ^{13}C NMR spectrum of the racemic mixture of 8 are due to the diastereomeric effect,[26] the syn isomer can be clearly distinguished from the anti isomer. The chemical shifts of 16-Me and 17-Me of compound 8 were in good agreement with those of (6*R*,10*R*)-8, as given in Table II. Thus, the relative configuration between C-6 and C-10 of compound 8 was confirmed to be syn and the configuration at C-10 of compound 8 which originates from C-35 of 4, should be

(26) Dalling, D. K.; Pugmire R. J.; Grant, D. M.; Hull, W. E. *Magn. Reson. Chem.* **1986**, *24*, 191–198.

Table II. ^{13}C NMR Chemical Shifts of 8, (6*R*,10*R*)-8, and the Racemic Mixture of 8

position	8	(6*R*,10*R*)-8	racemic mixture of 8
1	29.84	29.89	29.83
2	209.33	209.47	209.15
3	44.17	44.15	44.09
4	21.47	21.43	21.40
5	36.53	36.49	36.49, 36.57
6	32.70	32.68	32.66
7	37.25	37.23	37.18
8	24.44	24.45	24.42
9	37.31	37.29	37.26
10	32.81	32.80	32.77
11	37.43	37.41	37.38
12	24.81	24.79	24.79
13	39.40	39.37	39.37
14	27.99	27.99	27.96
15	22.62	22.63	22.63
16	19.60	19.58	19.52, 19.58
17	19.76	19.76	19.67, 19.73
18	22.73	22.75	22.72

R. Consequently, the structure of glycinoprenol-10 (4) was established to be (31*R*,35*R*)-(2*Z*,6*Z*,10*Z*,14*Z*,18*Z*,22*Z*,-26*E*)-3,7,11,15,19,23,27,31,35,39-decamethyl-2,6,10,14,18,-22,26-tetracontaheptaen-1-ol.

Glycinoprenol-9 (2) and glycinoprenol-11 (6) showed a molecular ion peak at *m/z* 636.6144 ($C_{45}H_{80}O$) and 772.7436 ($C_{55}H_{96}O$), respectively. These mass spectral data indicated that glycinoprenol-9 (2) and glycinoprenol-11 (6) are C_{45} and C_{55} homologues of 4, respectively. This indication was supported by similarity of the ^1H NMR spectra of 2 and 6 to that of 4, except for the integral values of the signals at δ 1.68, 1.93–2.10, and 5.08–5.15, which are assigned to the methyl, methylene, and olefinic protons of the internal (*Z*)-prenyl residues, respectively. The structures of 2 and 6 were further supported by similarity of the ^{13}C NMR spectra among compounds 2, 4, and 6 (Table I). On ozonolysis, both compounds 2 and 6 gave compound 8, which was identified by the GLC co-injection analysis, the CD method, IR, ^1H NMR, and ^{13}C NMR spectroscopies, and EI-mass spectrometry. The findings clearly indicate that glycinoprenol-9 (2), glycinoprenol-10 (4), and glycinoprenol-11 (6) have the same phytyl residue and differ in the number of internal (*Z*)-prenyl residues.

The contents of glycinoprenols and ficaprenols in the leaves of soybean rose up gradually in 10 weeks after germination, and their ultimate contents reached 0.08% and 0.21% of the fresh leaves, respectively, just before the leaves turned yellow.

So far, the polyprenols having a geranylgeranyl residue, a farnesyl residue, or two saturated prenyl residues at the ω-end of their prenyl chain have been isolated. Three novel polyprenols, glycinoprenol-9, -10, and -11, isolated from the leaves of soybean were proved to comprise a phytyl residue, four to six (*Z*)-prenyl residues, and a *Z* α-terminal residue aligned in that order, as described above. It is for the first time that occurrence of the C_{45}-, C_{50}-, and C_{55}-polyprenols having the phytyl residue was demonstrated.

Experimental Section

^1H NMR and ^{13}C NMR spectra were obtained with JEOL JNM GSX-270 and JNM GSX-400 spectrometers at 270.2 and 399.8 MHz for ^1H NMR and 67.9 and 100.5 MHz for ^{13}C NMR. Measurements were made in $CDCl_3$ at 27°C, and the 7.26 ppm resonance of residual $CHCl_3$ and 77.0 ppm of $CDCl_3$ were used as internal references for ^1H NMR and ^{13}C NMR, respectively. Mass spectra were obtained with a Hitachi M-80B GC double-focusing mass spectrometer operating at 70 eV. GC–mass spectra were recorded on the same spectrometer using an OV-1 glass-fused capillary column (0.2 mm × 50 m). The analytical GLC was carried out with a Shimadzu GC-15A gas chromatograph inter-

faced with a Shimadzu CR3A integrator. CD spectra were recorded on a JASCO J-600 spectropolarimeter. Opitcal rotation was measured with a JASCO DIP-360 digital polarimeter. The optical rotations of glycinoprenols (**2**, **4**, and **6**) and compound **8** obtained by ozonolysis of glycinoprenols could not be measured because of their small amount.

Isolation and Purification of Polyprenols. The leaves (1.85 kg) of soybean, *G. max*, were collected at the beginning of September (in 18 weeks after germination) and immersed in MeOH (20 L) at room temperature for 2 weeks. The MeOH extract was concentrated to 300 mL. The solution was diluted with H_2O (300 mL) and extracted with hexane. Removal of the solvent from the hexane solution gave a brown viscous oil (40.0 g). The crude oil was subjected to silica gel column chromatography using benzene as eluent to give a polyprenol fraction (6.08 g). The polyprenol fraction was subjected to HPLC analysis using a Wakopak C18 column (4.6 mm i.d. × 150 mm), and it showed six peaks as shown in Figure 1. Separation of each component was carried out by means of the reversed-phase HPLC on a Zorbax-ODS column (21.2 mm i.d. × 250 mm) with hexane–MeOH (1:4). Each component obtained was repeatedly purified by reversed-phase HPLC on a Wakopak C18 column (7.5 mm i.d. × 250 mm) with hexane–MeOH (1:4) to give 231, 16, 848, 80, 24, and 14 mg of pure compounds **1**–**6**. The content of the polyprenols varied with growth of the plant; age of leaves expressed in week after germination (wt % of glycinoprenols in the fresh leaves, wt % of ficaprenols in the fresh leaves): 2 (0.000 03, 0.003), 4 (0.000 07, 0.004), 6 (0.0003, 0.006), 8 (0.0003, 0.006), 10 (0.002, 0.03), 12 (0.006, 0.04), 14 (0.02, 0.08), 16 (0.03, 0.11), 18 (0.05, 0.20), 20 (0.06, 0.21), and 22 (0.08, 0.19).

Identification of Ficaprenol-10 (1), Ficaprenol-11 (3), and Ficaprenol-12 (5). Compounds **1**, **3**, and **5** showed the same retention times as the authentic samples of ficaprenol-10, -11, and -12 on reversed-phase HPLC (Wakopak C18 column), respectively. Identity was established by comparison of their IR, ^1H NMR, ^{13}C NMR, and high-resolution mass spectra with those of known specimens.

Glycinoprenol-9 (2): colorless oil; IR (neat) 3330 (OH) and 1665 cm^{-1} (C=C); HR MS m/z (relative intensity) 636.6144 [(3, M^+), $C_{45}H_{80}O$ requires m/z 636.6205] and 618.6157 [(13, $M - H_2O$), $C_{45}H_{78}$ requires m/z 618.6100]; ^1H NMR δ 0.84 (6 H, d, J = 6.5 Hz, CH_3), 0.86 (6 H, d, J = 6.6 Hz, CH_3), 1.00–1.52 (19 H, m, CH_2 and CH), 1.59 [3 H, d, J = 1.1 Hz, (*E*)-$C(CH_3)$=CH], 1.69 [12 H, s, (*Z*)-$C(CH_3)$=CH], 1.74 [3 H, dt, J = 1.3 and 0.9 Hz, (*Z*)-$C(CH_3)$=CH], 1.93–2.10 (22 H, m, CH_2CH_2), 4.09 (2 H, dd, J = 7.2 and 0.8 Hz, CH_2OH), 5.08–5.15 (5 H, m, >C=CH), and 5.44 [1 H, dt, J = 7.2 and 1.3 Hz, C(2)H]; ^{13}C NMR (Table I).

Glycinoprenol-10 (4): colorless oil; IR (neat) 3330 (OH) and 1662 cm^{-1} (C=C); HR MS m/z (relative intensity) 704.6833 [(1, M^+), $C_{50}H_{88}O$ requires m/z 704.6831] and 686.6699 [(2, $M - H_2O$), $C_{50}H_{86}$ requires m/z 686.6701]; ^1H NMR δ 0.84 (6 H, d, J = 6.6 Hz, CH_3), 0.86 (6 H, d, J = 6.7 Hz, CH_3), 1.00–1.52 (19 H, m, CH_2 and CH), 1.59 [3 H, br s, (*E*)-$C(CH_3)$=CH], 1.68 [15 H, s, (*Z*)-$C(CH_3)$=CH], 1.74 [3 H, br d, J = 1.3 Hz, (*Z*)-$C(CH_3)$=CH], 1.93–2.10 (26 H, m, CH_2CH_2), 4.09 (2 H, dd, J = 7.2 and 0.9 Hz, CH_2OH), 5.08–5.15 (6 H, m, >C=CH), and 5.44 [1 H, dt, J = 7.2 and 1.3 Hz, C(2)H]; ^{13}C NMR (Table I).

Glycinoprenol-11 (6): colorless oil; IR (neat) 3330 (OH) and 1663 cm^{-1} (C=C); HR MS m/z (relative intensity) 772.7436 [(2, M^+), $C_{55}H_{96}O$ requires m/z 772.7456] and 754.7280 [(6, $M - H_2O$), $C_{55}H_{94}$ requires m/z 754.7351]; ^1H NMR δ 0.84 (6 H, d, J = 6.4 Hz, CH_3), 0.86 (6 H, d, J = 6.6 Hz, CH_3), 1.00–1.52 (19 H, m, CH_2 and CH), 1.59 [3 H, d, J = 1.1 Hz, (*E*)-$C(CH_3)$=CH], 1.68 [18 H, s, (*Z*)-$C(CH_3)$=CH], 1.74 [3 H, dt, J = 1.4 and 0.9 Hz, (*Z*)-$C(CH_3)$=CH], 1.93–2.10 (30 H, m, CH_2CH_2), 4.09 (2 H, dd, J = 7.2 and 0.9 Hz, CH_2OH), 5.08–5.15 (7 H, m, >C=CH), and 5.44 [1 H, dt, J = 7.2 and 1.4 Hz, C(2)H]; ^{13}C NMR (Table I).

Ozonolysis of Glycinoprenol-10 (4). Compound **4** (15 mg) was ozonized in ethyl chloride (2 mL) at −78 °C with a stream of ozone in oxygen until a pale blue color persisted in the solution. Removal of the solvent at room temperature left an ozonide, to which 98% formic acid (0.5 mL) and 30% H_2O_2 (0.1 mL) were added. After the mixture had been allowed to stand for 4 h at room temperature, peroxides that remained were decomposed by the addition of powdered $FeSO_4 \cdot 7H_2O$ until evolution of gas stopped. After addition of Et_2O (20 mL), the mixture was filtered. To the filtrate was added 10% $NaHCO_3$ (10 mL). The ether layer was separated from the aqueous layer. The ether layer was evaporated to give a pale yellow oil (5 mg). The product was subjected to silica gel column chromatography (ether–hexane, 1:4) to give compound **8** (2 mg) as a colorless oil: over 99.9% pure on GLC; IR (neat) 1720 cm^{-1} (C=O); ^1H NMR δ 0.84 (6 H, d, J = 6.4 Hz, CH_3 × 2), 0.87 (6 H, d, J = 6.8 Hz, CH_3 × 2), 1.10–1.70 (19 H, m, CH_2 × 8 and CH × 3), 2.14 (3 H, s, CH_3CO), and 2.17 (2 H, t, $-CH_2CO-$); MS m/z (relative intensity) 268 (0.5, M^+), 253 (1, M − Me), 250 (3, $M - H_2O$), and 43 (100); CD (hexane) $\Delta\epsilon_{284}$ = +0.020 ± 0.002 (c 0.05); ^{13}C NMR (Table II).

The aqueous layer was acidified with 1 M HCl and extracted with ether. The ether extract was methylated with ethereal CH_2N_2. The methylated mixture was subjected to GLC analysis. The presence of methyl levulinate and dimethyl oxalate was confirmed by the co-injection analysis of the products with authentic samples.

(6*R*,10*R*)-8. Ozonolysis of natural (7*R*,11*R*)-phytol (**7**) (330 mg) [$[\alpha]^{25}_D$ +0.05° (neat) (lit.[25] $\alpha^{22.5}_D$ +0.03°)] was carried out by following the method described for the ozonolysis of **4**. The product was subjected to silica gel column chromatography (EtOAc–hexane, 1:9) to give (6*R*,10*R*)-**8** (249 mg): over 99.9% pure on GLC; $[\alpha]^{25}_D$ +0.59° (c 4.37, ether) [lit.[25] α^{23}_D +0.57° (neat)]; CD (hexane) $\Delta\epsilon_{288}$ = +0.015 ± 0.002 (c 0.05); ^{13}C NMR (Table II). IR, ^1H NMR, and mass spectral data were identical with those of **8**.

The Racemic Mixture of 8. 6,10,14-Trimethyl-5,9,13-pentadecatrien-2-one (**9**) (100 mg) was hydrogenated with H_2/5% Pd–C, and the hydrogenated product was subjected to silica gel column chromatography (EtOAc–hexane, 1:9) to give the racemic mixture of **8** (91 mg) as a colorless oil: ^{13}C NMR (Table II). IR, ^1H NMR, and mass spectral data were identical with those of **8** and (6*R*,10*R*)-**8**. GLC analysis of the racemic mixture of **8** was repeated three times, and the average relative area of peaks A and B on the chromatogram was determined to be 49.0% and 51.0%, respectively (Figure 3).

Ozonolysis of Glycinoprenol-9 (2) and Glycinoprenol-11 (6). According to the procedure for **4**, both ozonolyses of **2** and **6** were carried out to give **8**. The spectral data (CD, IR, ^1H NMR, ^{13}C NMR, and EI-MS) were identical with those of **8** derived from **4**.

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