Structure and Synthesis of Petrosynes, New Acetylenic Enol Ether Glycerides from the Okinawan Marine Sponge of the Genus *Petrosia*

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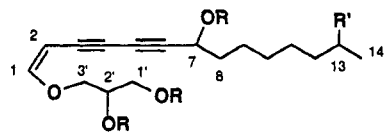
Acetylenic enol ether glycerides, **1** and **3**, were found in the Okinawan marine sponge of the genus *Petrosia*. The plane structures of these glycerides were deduced from spectroscopic analysis. Their complete structures were established by enantioselective total synthesis of all possible stereoisomers using (*R*)-1-*O*-benzylglycerol and its (*S*)-enantiomer, prepared from D-mannitol and L-ascorbic acid, respectively, as chiral building blocks. The synthesis involves the palladium(0)-catalyzed coupling reaction of bromo enol ether **9** with enediyne **21** as a key step. It became evident from the synthesis that the natural product **1** consisted of a mixture of (7*R*,2′*S*)-**24** (petrosyne Ia) and (7*S*,2′*S*)-**24** (petrosyne Ib), and the natural product **3** consisted of a mixture of (7*R*,2′*S*)-**28** (petrosyne IIa) and (7*S*,2′*S*)-**28** (petrosyne IIb).

Marine sponges are rich sources of long-chain acetylenic compounds,[1-11] some of which show significant biological activity such as antitumor activity. In the course of our investigation[12] on biologically active substances from Okinawan marine invertebrates, new acetylenic enol ether glycerides **1** and **3** possessing a conjugated enediyne system from the sponge (genus *Petrosia*) were found. The structures of these glycerides were elucidated based on spectroscopic analysis and enantioselective synthesis. A synthetic study indicated the diastereomers of the glyceride **1** (or its acetate **2**) having two chiral centers in the molecule not to be distinguishable by spectroscopic methods and the difference between these diastereomers to be evident in their MTPA esters. The natural glyceride **1** was shown to consist of a mixture of the diastereomers of (7*R*,2′*S*)-**24** and (7*S*,2′*S*)-**24**, and the natural glyceride **3** was also shown to consist of a mixture of the diastereomers of (7*R*,2′*S*)-**28** and (7*S*,2′*S*)-**28**.



1 R=R'=H
2 R=Ac, R'=H
3 R=H, R'=Me
4 R=Ac, R'=Me

Frozen specimens of the sponge of the genus *Petrosia*[13] (1.1 kg), collected on the coral reef of Ishigaki Island, were extracted with methanol. The ethyl acetate soluble portion (0.6 g) of the methanol extract was chromatographed on a silica gel column, giving four fractions. Fraction 3 obtained by elution with hexane–ethyl acetate (1:1) was further purified by silica gel column chromatography to give petrosynol, an antimicrobial polyacetylenic alcohol (120 mg) isolated from the Okinawan sponge (genus *Petrosia*) by Fusetani *et al.*[5] Fraction 4 obtained by elution with ethyl acetate was repeatedly chromatographed on a silica gel column to give a mixture of glycerides (7 mg). These compounds were fairly unstable and further separation using even HPLC failed to give good results, and thus the glyceride mixture was acetylated with acetic anhydride in pyridine followed by HPLC separation (silica gel, hexane:ethyl acetate = 3:1 as an eluent) to give acetate **4** (1 mg, $[\alpha]_D$ −9.1°, a colorless oil) and **2** (1 mg, $[\alpha]_D$ −9.8°, a colorless oil) in this order. These acetates were more stable than the natural glycerides, so that structure elucidation was possible using these acetates whose chromatographic and spectroscopic properties appeared to show each acetate as a single compound.

The molecular formula $C_{23}H_{32}O_7$ of **2** was determined by high-resolution mass measurement. IR absorption at 1746 cm^{-1} and ^1H NMR (Table I) signals of three acetoxy groups [δ 2.08 (3H, s), 2.09 (3H, s), and 2.10 (3H, s)] indicated **2** to be a triacetate, showing the natural glyceride **1** to be the corresponding triol owing to absence of ester groups in **1** and hydroxy groups in **2**. The glyceridic structure of $-OCH_2CH(OAc)CH_2OAc$ in **2** was suggested by analysis of ^1H and ^{13}C NMR spectra of **2**: δ_H 4.19 (1H, dd), 4.36 (1H, dd), δ_C 71.5 (CH_2) for C-1′; δ_H 5.21 (1H, m), δ_C 64.5 (CH) or 69.8 (CH) for C-2′; δ_H 4.09 (1H, dd), 4.11 (1H, dd), δ_C 62.0 (CH_2) for C-3′. This ^1H coupling sequence was confirmed by ^1H NMR decoupling experiments, and the glyceridic structure was also supported by the mass spectrum of **2**. A strong peak at *m/z* 159 (relative intensity 52%) due to the fragment ion formed by cleavage of the carbon–oxygen bond at C-3′ was observed. NMR signals of δ_H 5.44 (1H, t) and δ_C 64.5 (CH) or 69.8 (CH) indicated

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(13) The sponge was identified by Prof. R. W. M. van Soest, Institute of Taxonomic Zoology, University of Amsterdam. The specimens are on deposit in his collection (registered no.; ZMA Por. 9341).

0022-3263/93/1958-5690$04.00/0

Table I. ^{1}H NMR Data[a] for 2, 4, (7*R*,2'*R*)-23, (7*R*,2'*S*)-24, and (7*R*,2'*R*)-24

2	4	(7*R*,2'*R*)-23	(7*R*,2'*S*)-23	(7*R*,2'*S*)-24	(7*R*,2'*R*)-24
0.87 (3H, t, *J* = 6.6, H-14)	0.87 (6H, d, *J* = 6.6, H-14, H-15)	0.88 (3H, t, *J* = 7.0, H-14)	0.88 (3H, t, *J* = 7.0, H-14)	0.88 (3H, t, *J* = 7.1, H-14)	0.88 (3H, t, *J* = 7.1, H-14)
1.28 (8H, m, H-10–H-13)	1.28 (7H, m, H-10–H-13)	1.28 (8H, m, H-10–H-13)	1.28 (8H, m, H-10–H-13)	1.28 (8H, m, H-10–H-13)	1.28 (8H, m, H-10–H-13)
1.43 (2H, m, H-9)	1.43 (2H, m, H-9)	1.43 (2H, m, H-9)	1.43 (2H, m, H-9)	1.44 (2H, m, H-9)	1.44 (2H, m, H-9)
1.77 (2H, m, H-8)	1.77 (2H, m, H-8)	1.77 (2H, m, H-8)	1.77 (2H, m, H-8)	1.71 (2H, m, H-8)	1.71 (2H, m, H-8)
2.08 (3H, s, OAc)	2.08 (3H, s, OAc)	2.08 (3H, s, OAc)	2.07 (3H, s, OAc)	3.69 (1H, dd, *J* = 5.1, 11.5, H-1')	3.69 (1H, dd, *J* = 5.1, 11.5, H-1')
2.09 (3H, s, OAc)	2.09 (3H, s, OAc)	2.09 (3H, s, OAc)	2.08 (3H, s, OAc)		
2.10 (3H, s, OAc)	2.10 (3H, s, OAc)	2.10 (3H, s, OAc)	2.10 (3H, s, OAc)	3.77 (1H, dd, *J* = 3.7, 11.5, H-1')	3.77 (1H, dd, *J* = 3.7, 11.5, H-1')
4.09 (1H, dd, *J* = 5.4, 11.5, H-3')	4.09 (1H, dd, *J* = 5.5, 11.5, H-3')	4.09 (1H, dd, *J* = 5.4, 11.5, H-3')	4.09 (1H, dd, *J* = 5.4, 11.5, H-3')	3.99 (1H, m, H-2')	3.99 (1H, m, H-2')
4.11 (1H, dd, *J* = 4.8, 11.5, H-3')	4.11 (1H, dd, *J* = 4.8, 11.5, H-3')	4.11 (1H, dd, *J* = 4.8, 11.5, H-3')	4.11 (1H, dd, *J* = 4.9, 11.5, H-3')	4.02 (1H, dd, *J* = 5.9, 10.3, H-3')	4.04 (1H, dd, *J* = 3.8, 10.2, H-3')
4.19 (1H, dd, *J* = 5.6, 12.1, H-1')	4.19 (1H, dd, *J* = 5.6, 12.1, H-1')	4.19 (1H, dd, *J* = 5.6, 12.1, H-1')	4.19 (1H, dd, *J* = 5.6, 12.1, H-1')	4.05 (1H, dd, *J* = 3.9, 10.3, H-3')	4.06 (1H, dd, *J* = 3.8, 10.2, H-3')
4.36 (1H, dd, *J* = 4.2, 12.1, H-1')	4.36 (1H, dd, *J* = 4.2, 12.1, H-1')	4.36 (1H, dd, *J* = 4.2, 12.1, H-1')	4.36 (1H, dd, *J* = 4.2, 12.1, H-1')	4.46 (1H, t, *J* = 6.6, H-7)	4.46 (1H, t, *J* = 6.6, H-7)
4.60 (1H, d, *J* = 6.4, H-2)	4.60 (1H, d, *J* = 6.4, H-2)	4.60 (1H, d, *J* = 6.4, H-2)	4.60 (1H, d, *J* = 6.4, H-2)	4.61 (1H, d, *J* = 6.4, H-2)	4.61 (1H, d, *J* = 6.4, H-2)
5.21 (1H, m, H-2')	5.21 (1H, m, H-2')	5.21 (1H, m, H-2')	5.21 (1H, m, H-2')	6.53 (1H, d, *J* = 6.4, H-1)	6.53 (1H, d, *J* = 6.4, H-1)
5.44 (1H, t, *J* = 6.7, H-7)	5.44 (1H, t, *J* = 6.7, H-7)	5.44 (1H, t, *J* = 6.7, H-7)	5.44 (1H, t, *J* = 6.7, H-7)		
6.43 (1H, d, *J* = 6.4, H-1)	6.43 (1H, d, *J* = 6.4, H-1)	6.43 (1H, d, *J* = 6.4, H-1)	6.43 (1H, d, *J* = 6.4, H-1)		

[a] ^{1}H NMR spectra were measured at 500 MHz in $CDCl_3$. Chemical shifts are given in δ (ppm) based on $CHCl_3$ (7.26 ppm). *J* values in parentheses are expressed in Hz.

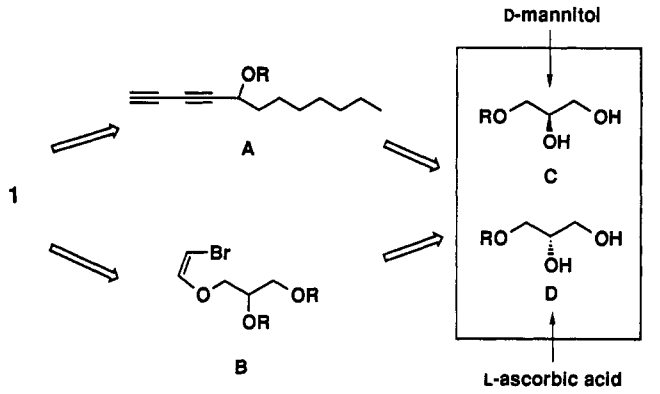


Figure 1. Synthetic strategy.

the remaining CHOAc group of **2** to be situated at an allylic position of a multiple bond.

An enol ether moiety –CH=CHO– was shown to be present by the low-field ^{1}H and ^{13}C signals at C-1 [δ_H 6.43 (1H, d), δ_C 158.4 (CH)] and the high-field signals at C-2 [δ_H 4.60 (1H, d), δ_C 85.2 (CH)]. The *Z* geometry of the double bond was indicated by the small coupling constant (*J* = 6.4 Hz) between H-1 and H-2. The number (7) of oxygen atoms in **2** indicated the enol ether to possibly be linked with the glyceridic moiety, which would then give the extended partial structure, –CH=CHOCH$_2$CH(OAc)-CH$_2$OAc.

Two acetylenic bonds in **2** were shown present by the IR absorptions (2237, 2149 cm^{-1}) and ^{13}C signals [δ_C 70.2 (C), 73.4 (C), 76.8 (C), 79.7 (C)]. Characteristic UV absorptions [223 (log ε 4.30), 250 (sh, log ε 3.79), 260 (log ε 3.86), 276 (log ε 3.94), 291 (log ε 3.85)] are related to those of hept-5-ene-1,3-diyne,[14] thus leading to a conjugated enediyne structure of –C≡CC≡CC=C–. Since there is only one carbon–carbon double bond in **2**, the double bond in the enediyne system should overlap with that of the previously mentioned enol ether system, leading to the extended partial structure, –C≡CC≡CCH=CHOCH$_2$-CH(OAc)CH$_2$OAc. NMR data (Table I) for the remaining protons and carbons ($C_{10}H_{19}O_2$) in **2** clearly showed the presence of a –CH(OAc)CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$ group, which should connect with the enediyne moiety leading to a plane structure of triacetate **2** and thus the natural product, **1**.

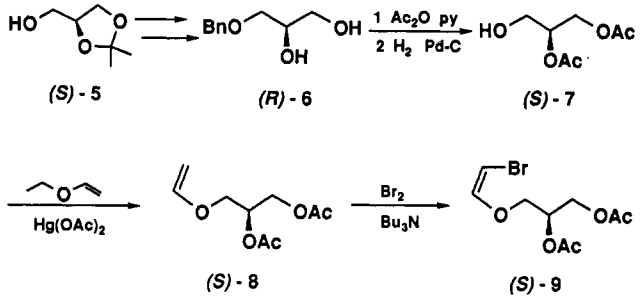
The molecular formula $C_{24}H_{34}O_7$ of acetate **4** was demonstrated by high-resolution mass measurement. ^{1}H NMR data of **4** (Table I) are nearly identical with those for **2** except for the signal at δ 0.87 (6H, d, *J* = 6.6 Hz) ppm instead of the methyl signal at δ 0.87 (3H, t) ppm in **2**. This is consistent with replacing the terminal ethyl group of **2** with an isopropyl group in **4**, leading to the plane structure of triacetate **4** and thus the natural product, **3**.

Compounds **1**–**4** were obtained in very limited amounts and unstable, and thus the stereochemistry of the two chiral centers in these compounds was determined by enantioselective total synthesis. The synthesis of all possible stereoisomers of **1** as shown in Figure 1 was conducted by coupling of chiral diyne **A** with chiral bromo enol ether **B** obtainable from chiral glycerol derivatives **C** and **D** prepared from D-mannitol or L-ascorbic acid.

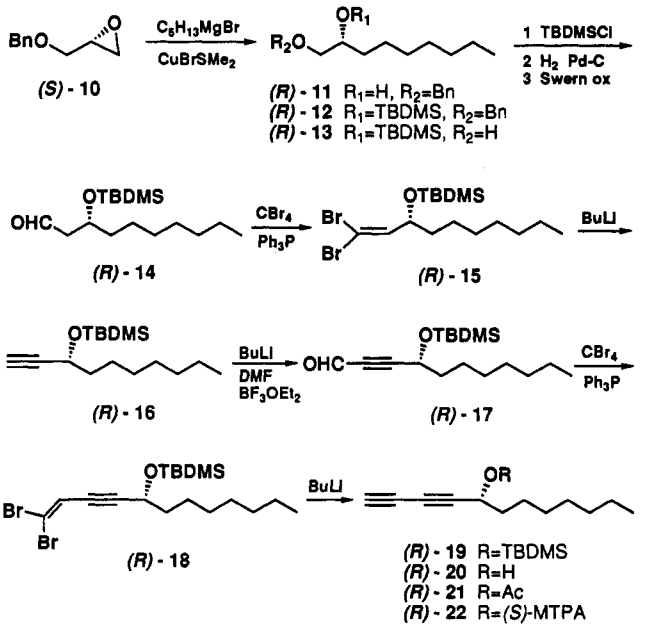
Chiral bromo enol ether (*S*)-**9** was synthesized as shown in Scheme I. (*R*)-1-*O*-Benzylglycerol [(*R*)-**6**],[15] obtained

(14) Jones, E. R. H.; Whiting, M. C.; Armitage, J. B.; Cook, L.; Entwistle, N. *Nature* **1951**, *168*, 900.

Scheme I



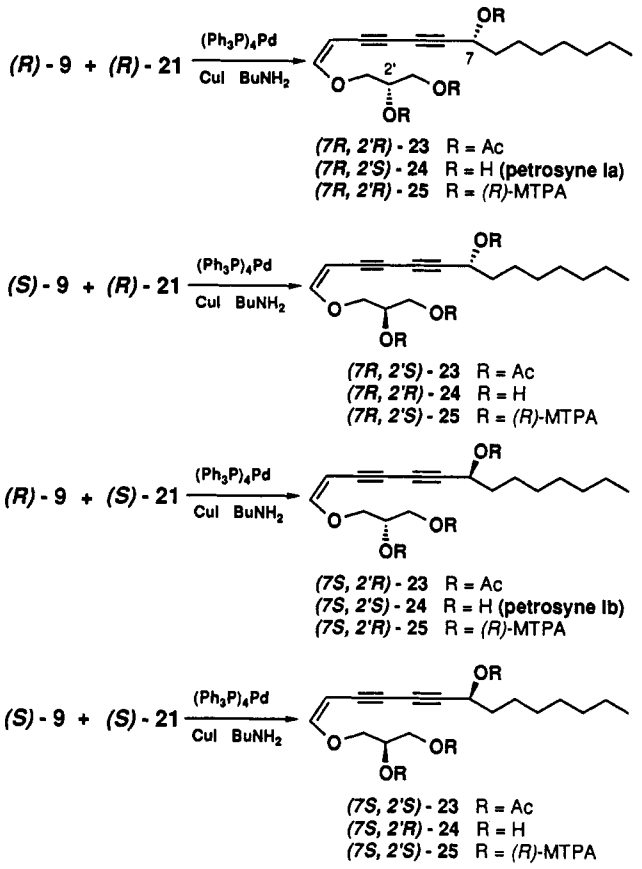
Scheme II



from D-mannitol *via* (*S*)-1,2-*O*-isopropylideneglycerol [(*S*)-**5**], was acetylated with acetic anhydride followed by hydrogenation over 10% palladium on carbon to give an alcohol (*S*)-**7** in 98% overall yield. (*S*)-**7** was then treated with ethyl vinyl ether in the presence of mercury(II) acetate to give an enol ether (*S*)-**8** in 89% yield. The bromination[16] of (*S*)-**8** in the presence of tributylamine gave a *Z*-bromoolefin (*S*)-**9** (50% yield, $[\alpha]_D$ +14.3°) along with an *E*-bromoolefin (22% yield). The desired *Z*-configuration of (*S*)-**9** was determined from its small ^1H coupling constant (J = 4.2 Hz) between the olefinic protons. Similarly, the enantiomeric (*R*)-bromoolefin (*R*)-**9** ($[\alpha]_D$ −12.2°) was synthesized from (*S*)-**6** prepared from L-ascorbic acid *via* (*R*)-1,2-*O*-isopropylideneglycerol [(*R*)-**5**].[17]

Chiral diyne (*R*)-**21** was synthesized as shown in Scheme II. The Grignard reaction of the (*S*)-epoxide (*S*)-**10**[18] prepared from (*R*)-**6** gave an alcohol (*R*)-**11** in 95% yield. Protection of the secondary hydroxy group in (*R*)-**11** with a *tert*-butyldimethylsilyl group gave (*R*)-**12**, which was hydrogenolyzed over 10% palladium on carbon to give a primary alcohol (*R*)-**13** in 86% overall yield. The Swern oxidation of (*R*)-**13** gave an aldehyde (*R*)-**14** which was treated with carbon tetrabromide and triphenylphosphine[19] to give a dibromoolefin (*R*)-**15** in 78% overall yield.

Scheme III



(*R*)-**15** was converted to an acetylene (*R*)-**16** by treatment with butyllithium[19] in 99% yield. Formylation of (*R*)-**16** with butyllithium and DMF in the presence of boron trifluoride etherate gave an aldehyde (*R*)-**17** in 78% yield, which was converted to a diyne (*R*)-**19** ($[\alpha]_D$ +41.5°) *via* (*R*)-**18** by reactions similar to those for the conversion of (*R*)-**14** to (*R*)-**16** in 77% overall yield. Deprotection of the *tert*-butyldimethylsilyl group in (*R*)-**19** gave an alcohol (*R*)-**20** ($[\alpha]_D$ −6.3°) in 99% yield, which was converted to an acetate (*R*)-**21** ($[\alpha]_D$ +96.6°). The optical purity of (*R*)-**20** (an enantiomeric excess above 92%) was confirmed from measurement of the ^1H NMR spectrum of the (*S*)-MTPA ester (*R*)-**22** prepared by treating (*R*)-**20** with (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride in pyridine. Similarly, the enantiomeric acetate (*S*)-**21** ($[\alpha]_D$ −127.8°) was synthesized from (*R*)-**10**[20] obtained from L-ascorbic acid *via* (*S*)-**6**. The optical purity of (*S*)-**20** (an enantiomeric excess above 92%) was confirmed by the ^1H NMR spectrum of the (*S*)-MTPA ester (*S*)-**22**.

The coupling reaction of (*R*)-**9** and (*R*)-**21** induced by tetrakis(triphenylphosphine)palladium(0)[21] was conducted in the presence of copper(I) iodide and butylamine in DMF to give an endiyne (7*R*,2′*R*)-**23** ($[\alpha]_D$ +80.1°) in 27% yield as shown in Scheme III. The stereoisomers, (7*R*,2′*S*)-**23** ($[\alpha]_D$ +114.0°), (7*S*,2′*R*)-**23** ($[\alpha]_D$ −94.5°), and (7*S*,2′*S*)-**23** ($[\alpha]_D$ −42.8°),[22] were also synthesized by the palladium-(0)-induced coupling reactions of (*S*)-**9** and (*R*)-**21**, (*R*)-**9** and (*S*)-**21**, and (*S*)-**9** and (*S*)-**21**, respectively, in 11-30%

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(22) It is not clear why the absolute value of the optical rotation of the compound was smaller than that of its enantiomer.

yield. Unexpectedly, all four synthetic diastereomers had the same UV, ^{1}H NMR (Table I) and ^{13}C NMR spectra, and the spectral data of triacetate **2** derived from the natural product **1** coincided with those of the four synthetic triacetates. Furthermore, the spectral data of the triols, (7*R*,2′*S*)-**24** ([α]$_D$ +5.9°), (7*R*,2′*R*)-**24** ([α]$_D$ −6.8°), (7*S*,2′*S*)-**24** ([α]$_D$ +7.2°), and (7*S*,2′*R*)-**24** ([α]$_D$ −0.8°),[22] obtained by treating triacetates (7*R*,2′*R*)-**23**, (7*R*,2′*S*)-**23**, (7*S*,2′*R*)-**23**, and (7*S*,2′*S*)-**23** with lithium carbonate in methanol, respectively, were also the same (Table I).

The corresponding (*R*)-MTPA esters, (7*R*,2′*R*)-**25** ([α]$_D$ +58.0°), (7*R*,2′*S*)-**25** ([α]$_D$ +18.3°), (7*S*,2′*R*)-**25** ([α]$_D$ +44.7°), and (7*S*,2′*S*)-**25** ([α]$_D$ +13.7°), obtained by acylation of the triols with (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride in pyridine, respectively, each showed a different ^{1}H NMR spectrum (Table II). On comparison of the ^{1}H NMR spectrum of (7*R*,2′*R*)-**25** with that of (7*R*,2′*S*)-**25**, clear differences could be seen for the following protons: H-1 [6.10 (d) for (7*R*,2′*R*)-**25**, 6.28 (d) for (7*R*,2′*S*)-**25**], H-2 [4.49 (d) for (7*R*,2′*R*)-**25**, 4.58 (d) for (7*R*,2′*S*)-**25**], H-1′ [4.41 (dd) and 4.78 (dd) for (7*R*,2′*R*)-**25**, 4.38 (dd) and 4.63 (dd) for (7*R*,2′*S*)-**25**], H-2′ [5.49 (m) for (7*R*,2′*R*)-**25**, 5.51 (m) for (7*R*,2′*S*)-**25**], H-3′ [3.97 (dd) and 4.00 (dd) for (7*R*,2′*R*)-**25**, 4.07 (2H, d) for (7*R*,2′*S*)-**25**], two of the three methoxy protons [3.42 (s) and 3.49 (s) for (7*R*,2′*R*)-**25**, 3.40 (s) and 3.52 (s) for (7*R*,2′*S*)-**25**]. Differences were also observed between the ^{1}H NMR spectra of the MTPA esters having different configurations at C-7 and the same at C-2′, such as (7*R*,2′*R*)-**25** and (7*S*,2′*R*)-**25**; H-1 [6.10 (d) for (7*R*,2′*R*)-**25**, 6.09 (d) for (7*S*,2′*R*)-**25**], H-7 [5.63 (t) for (7*R*,2′*R*)-**25**, 5.60 (t) for (7*S*,2′*R*)-**25**], one of the three methoxy protons [3.57 (s) for (7*R*,2′*R*)-**25**, 3.53 (s) for (7*S*,2′*R*)-**25**]. The triacetate **2** was thus converted to alcohol **1** and then acylated to the corresponding (*R*)-MTPA ester. Comparison of the ^{1}H NMR spectrum of the MTPA ester from **1** with those of the synthetic MTPA esters indicated, surprisingly, that the MTPA ester from the natural product apparently consists of two esters, (7*R*,2′*R*)-**25** and (7*S*,2′*R*)-**25**, in a ratio of about 1:1. The natural product **1** is thus shown to be a diastereomeric mixture of (7*R*,2′*S*)-**24** and (7*S*,2′*S*)-**24** in a ratio of about 1:1. Although these natural compounds could not be isolated in pure form from the sponge, they were characterized by the corresponding synthetic compounds. Natural (7*R*,2′*S*)-**24** and (7*S*,2′*S*)-**24** were consequently designated as petrosyne Ia and Ib, respectively. Petrosyne Ia and Ib may possibly have originally been present in the sponge because no isomerization at the C-7 position could be detected during the usual treatment of synthetic compounds **15**–**25**.

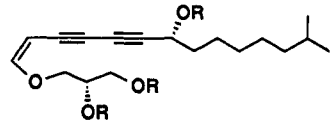
Triacetate **4** from the natural product was converted to the (*R*)-MTPA ester, whose ^{1}H NMR spectrum was shown to be closely related to those of the above MTPA esters derived from petrosyne Ia and Ib, thus indicating the MTPA ester from **4** to quite likely consist of two esters, (7*R*,2′*R*)-**26** and (7*S*,2′*R*)-**26**, in a ratio of about 1:1 (Experimental Section). Triacetate **4** may thus possibly consist of (7*R*,2′*R*)-**27** and (7*S*,2′*R*)-**27**, and the natural product **3** may also consist of (7*R*,2′*S*)-**28** and (7*S*,2′*S*)-**28**, named petrosyne IIa and IIb, respectively, in a ratio of about 1:1.

Acetylenic enol ether glycerides occur very rarely in nature. Although the yne dienol ether, (+)-raspailyne-A,[2] from the sponge *Raspailia pumila*, and two diyne enol ethers[10] from the sponge *Petrosia hebes* have been reported

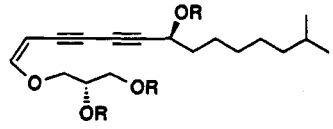
Table II. ^{1}H NMR Data[a] for MTPA Esters, (7*R*,2′*R*)-25, (7*R*,2′*S*)-25, (7*S*,2′*R*)-25, and (7*S*,2′*S*)-25, and MTPA Ester Mixture from the Natural Product

(7*R*,2′*R*)-25	(7*R*,2′*S*)-25	(7*S*,2′*R*)-25	(7*S*,2′*S*)-25	MTPA ester mixture from the natural product
0.87 (3H, t, *J* = 6.9, H-14)	0.87 (3H, t, *J* = 6.8, H-14)	0.88 (3H, t, *J* = 7.1, H-14)	0.88 (3H, t, *J* = 7.1, H-14)	0.88 (3H, t, *J* = 7.1, H-14)
				1.20–1.35 (m)
1.15–1.35 (10H, m, H-9–H-13)	1.15–1.35 (10H, m, H-9–H-13)	1.26 (8H, m, H-10–H-13)	1.27 (8H, m, H-10–H-13)	1.40–1.90 (m)[b]
		1.43 (2H, m, H-9)	1.42 (2H, m, H-9)	3.42 (6H, s, OMe)
1.77 (2H, m, H-8)	1.77 (2H, m, H-8)	1.85 (2H, m, H-8)	1.85 (2H, m, H-8)	3.49 (6H, s, OMe)
3.42 (3H, s, OMe)	3.40 (3H, s, OMe)	3.42 (3H, s, OMe)	3.40 (3H, s, OMe)	3.53 (3H, s, OMe for (7*S*,2′*R*)-25)
3.49 (3H, s, OMe)	3.52 (3H, s, OMe)	3.48 (3H, s, OMe)	3.52 (3H, s, OMe)	
3.57 (3H, s, OMe)	3.57 (3H, s, OMe)	3.53 (3H, s, OMe)	3.54 (3H, s, OMe)	3.57 (3H, s, OMe for (7*R*,2′*R*)-25)
3.97 (1H, dd, *J* = 4.6, 11.7, H-3′)	4.07 (2H, d, *J* = 5.5, H-3′)	3.97 (1H, dd, *J* = 4.6, 11.7, H-3′)	4.06 (2H, d, *J* = 5.5, H-3′)	3.96 (2H, dd, *J* = 4.6, 11.7, H-3′)
4.00 (1H, dd, *J* = 5.7, 11.7, H-3′)		4.00 (1H, dd, *J* = 5.8, 11.7, H-3′)		4.01 (2H, dd, *J* = 5.8, 11.7, H-3′)
4.41 (1H, dd, *J* = 5.5, 12.4, H-1′)	4.38 (1H, dd, *J* = 4.2, 12.4, H-1′)	4.41 (1H, dd, *J* = 5.5, 12.4, H-1′)	4.38 (1H, dd, *J* = 4.3, 12.3, H-1′)	4.41 (2H, dd, *J* = 5.4, 12.3, H-1′)
4.49 (1H, d, *J* = 6.4, H-2)	4.58 (1H, d, *J* = 6.4, H-2)	4.48 (1H, d, *J* = 6.4, H-2)	4.58 (1H, d, *J* = 6.4, H-2)	
4.78 (1H, dd, *J* = 3.4, 12.4, H-1′)	4.63 (1H, dd, *J* = 3.8, 12.4, H-1′)	4.78 (1H, dd, *J* = 3.4, 12.4, H-1′)	4.62 (1H, dd, *J* = 3.8, 12.3, H-1′)	4.48 (1H, d, *J* = 6.4, H-2 for (7*S*,2′*R*)-25)
5.49 (1H, m, H-2′)	5.51 (1H, m, H-2′)	5.49 (1H, m, H-2′)	5.50 (1H, m, H-2′)	4.49 (1H, d, *J* = 6.4, H-2 for (7*R*,2′*R*)-25)
5.63 (1H, t, *J* = 6.6, H-7)	5.64 (1H, t, *J* = 6.6, H-7)	5.60 (1H, t, *J* = 6.7, H-7)	5.60 (1H, t, *J* = 6.7, H-7)	4.78 (2H, dd, *J* = 3.6, 12.3, H-1′)
6.10 (1H, d, *J* = 6.4, H-1)	6.28 (1H, d, *J* = 6.4, H-1)	6.09 (1H, d, *J* = 6.4, H-1)	6.27 (1H, d, *J* = 6.4, H-1)	5.49 (2H, m, H-2′)
				5.60 (1H, t, *J* = 6.4, H-7 for (7*S*,2′*R*)-25)
7.30–7.55 (15H, m, phenyl H)	7.30–7.55 (15H, m, phenyl H)	7.30–7.55 (15H, m, phenyl H)	7.30–7.55 (15H, m, phenyl H)	5.63 (1H, t, *J* = 6.2, H-7 for (7*R*,2′*R*)-25)
				6.09 (1H, d, *J* = 6.4, H-1 for (7*S*,2′*R*)-25)
				6.10 (1H, d, *J* = 6.5, H-1 for (7*R*,2′*R*)-25)
				7.35–7.60 (30H, m, phenyl H)

[a] ^{1}H NMR spectra were measured at 400 MHz in $CDCl_3$. Chemical shifts are given in δ (ppm) based on $CHCl_3$ (7.26 ppm). *J* values in parentheses are expressed in Hz. [b] Signals overlap with that of water.



(7R, 2'R) - 26 R = (R) - MTPA
(7R, 2'R) - 27 R = Ac
(7R, 2'S) - 28 R = H (petrosyne IIa)



(7S, 2'R) - 26 R = (R) - MTPA
(7S, 2'R) - 27 R = Ac
(7S, 2'S) - 28 R = H (petrosyne IIb)

as compounds related to petrosynes, their stereostructures remain to be determined. The synthetic petrosyne Ia [(7*R*,2'*S*)-24] showed a moderate antifungal activity at a concentration of 1 mg/mL toward *Trichophyton mentagrophytes* and *Staphylococcus aureus*.

Experimental Section

^{1}H NMR (400 and 500 MHz) and ^{13}C NMR (100 and 125 MHz) spectra were recorded in $CDCl_3$ solutions. ^{1}H chemical shifts are given in δ (ppm) based on $CHCl_3$ (7.26 ppm). ^{13}C chemical shifts are given in δ (ppm) based on the solvent used (77.1 ppm for $CDCl_3$). Numbers of attached protons for ^{13}C signals were determined by DEPT experiments. EIMS spectra were obtained at 70 eV.

Extraction and Isolation. Wet specimens[13] of the sponge of the genus *Petrosia* (1.1 kg), collected on the coral reef of Ishigaki Island (Okinawa, Japan) in Nov 1988, were extracted with MeOH. The MeOH extract was suspended in water and extracted with EtOAc. The EtOAc-soluble portion (0.6 g) was chromatographed on a silica gel column. Stepwise elution with hexane–EtOAc (10:1, 5:1, and then 1:1) and EtOAc gave four fractions. The third fraction obtained by elution with hexane–EtOAc (1:1) was further purified by repeated silica gel column chromatography to give petrosynol[5] (120 mg, colorless oil). The fourth fraction (20 mg) obtained by elution with EtOAc was further subjected to repeated silica gel column chromatography (hexane:EtOAc = 1:2) to give a mixture of enediynes as an unstable colorless oil (7 mg).

The mixture was treated with acetic anhydride (1.0 mL) in pyridine (2.0 mL) at room temperature overnight. The reaction mixture was concentrated under reduced pressure. The residue obtained was chromatographed on a silica gel column (hexane: EtOAc = 3:1 as an eluent) to give crude acetate (7 mg), which was subjected to normal-phase HPLC (silica gel, hexane:EtOAc = 3:1 as an eluent, UV 254 nm, 10 mL/min for flow rate) to give triacetate **4** (1 mg) and **2** (1 mg) in this order each as a colorless oil.

Triacetate 2 (a 1:1 mixture of petrosyne Ia triacetate and Ib triacetate): $[\alpha]_D$ −9.8° (*c* 0.16, MeOH); EIMS *m/z* 420 (M^+); HREIMS M^+ *m/z* obsd 420.2129, $C_{23}H_{32}O_7$ required 420.2148; IR (film) 2237, 2149, 1746 cm^{-1}; UV (EtOH, log ϵ) 223 (4.30), 250 (sh, 3.79), 260 (3.86), 276 (3.94), 291 (3.85) nm; ^{1}H NMR (500 MHz) see Table I; ^{13}C NMR (125 MHz)[23] δ 14.1 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 21.0 (CH_3), 22.6 (CH_2), 25.0 (CH_2), 29.1 ($2CH_2$), 31.7 (CH_2), 34.6 (CH_2), 62.0 (CH_2), 64.5 (CH), 69.8 (CH), 70.2 (C), 71.5 (CH_2), 73.4 (C), 76.8 (C), 79.7 (C), 85.2 (CH), 158.4 (CH).

Triacetate 4 (a mixture of petrosyne IIa triacetate and IIb triacetate): $[\alpha]_D$ −9.1° (*c* 0.09, MeOH); EIMS *m/z* 434 (M^+); HREIMS M^+ *m/z* obsd 434.2275, $C_{24}H_{34}O_7$ required 434.2305; IR (film) 2237, 2149, 1746 cm^{-1}; UV (EtOH, log ϵ) 223 (4.34), 250 (sh, 3.69), 260 (3.90), 276 (4.01), 292 (3.92) nm; ^{1}H NMR (500 MHz) see Table I.

(23) The carbonyl signals could not be observed because of the small amount of the sample.

(*S*)-1,2-*O*-Diacetylglycerol [(*S*)-7]. To a stirred solution of (*R*)-1-*O*-benzylglycerol[15] [(*R*)-6, 7.4 g, 40.7 mmol] in pyridine (15 mL) was added acetic anhydride (8 mL, 84.9 mmol), and the mixture was stirred for 12 h at room temperature. The mixture was concentrated under reduced pressure to give a residue, which was chromatographed on a silica gel column (hexane:EtOAc = 3:1 as an eluent) to give (*S*)-3-*O*-benzyl-1,2-*O*-diacetylglycerol (11.0 g, 99% yield).

A mixture of (*S*)-3-*O*-benzyl-1,2-*O*-diacetylglycerol (10 g, 37.6 mmol), 10% palladium on carbon (1 g), and MeOH (50 mL) was vigorously stirred under a hydrogen atmosphere for 10 h at room temperature. The mixture was diluted with EtOAc and passed through a Celite short column. The eluate was concentrated under reduced pressure and the residue purified by silica gel column chromatography (eluted with hexane:EtOAc = 3:1 and then 1:2) to give (*S*)-1,2-*O*-diacetyl glycerol [(*S*)-7] (6.6 g, 99% yield): colorless oil; $[\alpha]_D$ +8.3° (*c* 0.4, $CHCl_3$); CIMS *m/z* 175 (M^+ − H), 145 ($M^+ - CH_2OH$); HREIMS $M^+ - CH_2OH$ *m/z* obsd 145.0513, $C_6H_9O_4$ required 145.0501; IR (film) 3462, 1747 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.08 (3H, s), 2.11 (3H, s), 3.75 (2H, d, *J* = 4.6 Hz), 4.23 (1H, dd, *J* = 4.5, 12.0 Hz), 4.32 (1H, dd, *J* = 4.4, 12.0 Hz), 5.08 (1H, m).

(*S*)-1,2-*O*-Diacetyl-3-*O*-vinylglycerol [(*S*)-8]. To a stirred solution of (*S*)-7 (6.5 g, 36.9 mmol) in ethyl vinyl ether (32 mL, 335 mmol) was added mercury(II) acetate (765 mg, 2.40 mmol) under an argon atmosphere. After being refluxed for 12 h, the mixture was cooled to room temperature. K_2CO_3 (6 g, 43.4 mmol) was then added, and the mixture was stirred for 30 min at room temperature. The mixture was passed through a silica gel short column (6 g), and the column was eluted with a mixed solvent of hexane–EtOAc (1:1). The eluate was concentrated under reduced pressure and the residue purified by silica gel column chromatography (eluted with hexane:EtOAc = 3:1, 2:1, and then 1:2) to give (*S*)-1,2-*O*-diacetyl-3-*O*-vinylglycerol [(*S*)-8] (4.0 g, 89% yield based on the consumed starting compound): colorless oil; $[\alpha]_D$ +14.4° (*c* 1.07, $CHCl_3$); EIMS *m/z* 203 (M^+ + 1), 159 ($M^+ - OCH{=}CH_2$); HREIMS $M^+ - OCH{=}CH_2$ *m/z* obsd 159.0693, $C_7H_{11}O_4$ required 159.0657; ^{1}H NMR (400 MHz) δ 2.00 (3H, s), 2.02 (3H, s), 3.77 (2H, d, *J* = 5.1 Hz), 3.98 (1H, dd, *J* = 2.4, 6.8 Hz), 4.12 (1H, dd, *J* = 6.1, 12.0 Hz), 4.15 (1H, dd, *J* = 2.4, 14.3 Hz), 4.28 (1H, dd, *J* = 4.0, 12.0 Hz), 5.20 (1H, m), 6.38 (1H, dd, *J* = 6.8, 14.3 Hz).

(*S*)-3-*O*-[(*Z*)-1-(2-Bromoethenyl)]-1,2-*O*-diacetylglycerol [(*S*)-9]. To a stirred cold (−78 °C) solution of (*S*)-8 (1.0 g, 4.95 mmol) in dry CH_2Cl_2 (15 mL) was added bromine (0.48 mL, 5.03 mmol) in dry CH_2Cl_2 (5 mL) during 30 min under an argon atmosphere. Tributylamine (1.3 mL, 5.46 mmol) was then added at −78 °C, and the temperature of the mixture was raised to room temperature. After the mixture was stirred for 12 h at room temperature, saturated $NaHCO_3$ solution was added, and the mixture was extracted with ether. The ethereal solution was washed with H_2O and saturated NaCl, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was chromatographed on a silica gel column (eluted with hexane: EtOAc = 5:1, 3:1, and then 1:1) to give (*S*)-3-*O*-[(*Z*)-1-(2-bromoethenyl)]-1,2-*O*-diacetylglycerol [(*S*)-9] (694 mg, 50% yield) and its *E*-isomer (305 mg, 22% yield).

(*S*)-9: colorless oil; $[\alpha]_D$ +14.3° (*c* 1.41, $CHCl_3$); EIMS *m/z* 281, 283 (M^+ + 1, 1:1); HREIMS M^+ *m/z* obsd 279.9951, $C_9H_{13}O_5{}^{79}Br$ required 279.9946; ^{1}H NMR (400 MHz) δ 2.07 (3H, s), 2.09 (3H, s), 4.02 (1H, dd, *J* = 5.4, 11.4 Hz), 4.05 (1H, dd, *J* = 4.2, 12.0 Hz), 4.19 (1H, dd, *J* = 5.7, 12.0 Hz), 4.37 (1H, dd, *J* = 4.2, 12.0 Hz), 5.18 (1H, d, *J* = 4.2 Hz), 5.22 (1H, m), 6.58 (1H, d, *J* = 4.2 Hz).

(*S*)-1-*O*-Benzylglycerol [(*S*)-6]. To a stirred solution of (*R*)-1,2-*O*-isopropylideneglycerol[17] [(*R*)-5, (4.7 g, 35.6 mmol)] in a mixed solvent of dry THF and DMF (4:1, 40 mL) were added sequentially benzyl bromide (4.6 mL, 38.7 mmol) and sodium hydride (1.0 g, 41.6 mmol) under an argon atmosphere. After the solution was stirred for 12 h at room temperature, excess MeOH was added, and the mixture was stirred for 30 min. The mixture was diluted with ether, washed with H_2O and saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was used for the following hydrolysis. A mixture of the residue in a mixed solvent of AcOH and H_2O (4:1, 100 mL) was stirred for 12 h at room temperature.

The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (eluted with hexane:EtOAc = 3:1 and then EtOAc) to give (*S*)-1-*O*-benzylglycerol [(*S*)-**6**] (5.8 g, 89% yield): colorless oil; $[\alpha]_D$ +2.7° (*c* 0.73, $CHCl_3$).

(*R*)-1,2-*O*-Diacetylglycerol [(*R*)-7]. To a stirred solution of (*S*)-**6** (1.7 g, 9.34 mmol) in pyridine (7.5 mL) was added acetic anhydride (4.3 mL, 45.5 mmol), and the mixture was stirred for 12 h at room temperature. The mixture was concentrated under reduced pressure to give the residue, which was chromatographed on a silica gel column (hexane:EtOAc = 3:1 as an eluent) to give (*R*)-3-*O*-benzyl-1,2-*O*-diacetylglycerol (2.5 g, 99% yield).

(*R*)-3-*O*-Benzyl-1,2-*O*-diacetylglycerol (2.4 g) was converted into (*R*)-1,2-*O*-diacetylglycerol [(*R*)-**7**] (1.6 g, 99% yield) under conditions similar to those for the synthesis of (*S*)-**7**. (*R*)-**7**: colorless oil; the ^1H NMR spectrum was identical with that of (*S*)-**7**.

(*R*)-3-*O*-[(*Z*)-1-(2-Bromoethenyl)]-1,2-*O*-diacetylglycerol [(*R*)-9]. The compound (*R*)-**7** (1.5 g) was converted into (*R*)-3-*O*-[(*Z*)-1-(2-bromoethenyl)]-1,2-*O*-diacetylglycerol [(*R*)-**9**] (636 mg, 44.5% overall yield) *via* the vinyl ether (*R*)-**8** under conditions similar to those for the synthesis of (*S*)-**9**. (*R*)-**9**: colorless oil; $[\alpha]_D$ −12.2° (*c* 0.77, $CHCl_3$); the ^1H NMR spectrum was identical with that of (*S*)-**9**.

(*R*)-1-*O*-Benzylnonane-1,2-diol [(*R*)-11]. To a stirred cold (−78 °C) solution of copper(I) bromide–dimethyl sulfide complex (319 mg, 1.55 mmol) in dry THF were added sequentially a 0.8 M solution of hexylmagnesium bromide in THF (58.1 mL, 46.4 mmol) and a solution of (*S*)-**10**[18] (5.1 g, 31.1 mmol) in dry THF (10 mL) under an argon atmosphere. After being stirred for 30 min at −78 °C, the mixture was diluted with ether, washed with saturated NH_4Cl solution, H_2O, and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (eluted with hexane:EtOAc = 20:1, 10:1, and then 8:1) to give (*R*)-1-*O*-benzylnonane-1,2-diol [(*R*)-**11**] (7.4 g, 95% yield): colorless oil $[\alpha]_D$ −3.6° (*c* 1.03, $CHCl_3$): EIMS *m/z* 250 (M^+); HREIMS M^+ *m/z* obsd 250.1937, $C_{16}H_{26}O_2$ required 250.1932; ^1H NMR (400 MHz) δ 0.88 (3H, t *J* = 6.5 Hz), 3.33 (1H, dd, *J* = 8.0, 9.4 Hz), 3.51 (1H, dd, *J* = 3.0, 9.4 Hz), 3.81 (1H, m), 4.56 (2H, s), 7.30 (5H, m).

(*R*)-1-*O*-Benzyl-2-*O*-(*tert*-butyldimethylsilyl)nonane-1,2-diol [(*R*)-12]. To a stirred solution of (*R*)-**11** (7.4 g, 29.6 mmol) in dry DMF (15 mL) was added sequentially imidazole (3.0 g, 44.1 mmol) and *tert*-butyldimethylsilyl chloride (4.9 g, 32.5 mmol) under an argon atmosphere. After being stirred for 10 h at room temperature, the mixture was diluted with ether, washed with H_2O and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (eluted with hexane:EtOAc = 30:1) to give (*R*)-1-*O*-benzyl-2-*O*-(*tert*-butyldimethylsilyl)nonane-1,2-diol [(*R*)-**12**] (10.1 g, 94% yield): colorless oil; $[\alpha]_D$ −10.4° (*c* 2.24, $CHCl_3$); EIMS *m/z* 307 ($M^+ - C_4H_9$); HREIMS $M^+ - C_4H_9$ *m/z* obsd 307.2181, $C_{18}H_{31}O_2Si$ required 307.2093; ^1H NMR (400 MHz) δ 0.04 (3H, s), 0.05 (3H, s), 0.88 (9H, s), 0.88 (3H, t, *J* = 7.7 Hz), 3.36 (1H, dd, *J* = 5.3, 9.6 Hz), 3.39 (1H, dd, *J* = 5.6, 9.6 Hz), 3.81 (1H, m), 4.52 (2H, s), 7.28–7.34 (5H, m).

(*R*)-2-*O*-(*tert*-Butyldimethylsilyl)nonane-1,2-diol [(*R*)-13]. A mixture of (*R*)-**12** (10.1 g, 27.7 mmol) in dry MeOH and 10% palladium on carbon (2 g) was vigorously stirred for 10 h at room temperature under a hydrogen atmosphere. The mixture was diluted with EtOAc and passed through a Celite short column. The eluate was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexane:EtOAc = 20:1 as an eluant) to give (*R*)-2-*O*-(*tert*-butyldimethylsilyl)nonane-1,2-diol [(*R*)-**13**] (7.0 g, 92% yield): colorless oil; $[\alpha]_D$ −6.9° (*c* 1.69, $CHCl_3$); EIMS *m/z* 243 ($M^+ - CH_2OH$), 217 ($M^+ - C_4H_9$); HREIMS $M^+ - CH_2OH$ *m/z* obsd 243.2148, $C_{14}H_{31}OSi$ required 243.2144; IR (film) 3392 cm^{-1}; ^1H NMR (400 MHz) δ 0.08 (6H, s), 0.88 (3H, t, *J* = 7.1 Hz), 0.90 (9H, s), 3.44 (1H, dd, *J* = 5.4, 11.0 Hz), 3.56 (1H, dd, *J* = 3.6, 11.0 Hz), 3.72 (1H, m).

(*R*)-3-[(*tert*-Butyldimethylsilyl)oxy]nonan-1-al [(*R*)-14]. To a stirred cold (−78 °C) solution of oxalyl chloride (12 mL, 138 mmol) in dry CH_2Cl_2 (200 mL) was added dry DMSO (12.6 mL, 178 mmol) under an argon atmosphere. After the solution was stirred for 10 min at −78 °C, a solution of (*R*)-**13** (5.4 g, 19.7 mmol) in dry CH_2Cl_2 (20 mL) was added, and the mixture was stirred for 15 min at −78 °C. After being stirred for 1 h further at −45 °C, the mixture was again cooled to −78 °C. Triethylamine (30 mL, 215 mmol) was then added, and the mixture was stirred for 30 min at −78 °C. The mixture was allowed to warm to 0 °C and stirred for 1 h further at this temperature. The mixture was diluted with C_6H_6–Et_2O (4:1), washed with H_2O and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure to give crude (*R*)-3-[(*tert*-butyldimethylsilyl)oxy]nonan-1-al [(*R*)-**14**, 5.3 g], which was used for the following reaction without any purification procedure. The sample for physical data was obtained by preparative TLC (hexane:EtOAc = 10:1 as a development solvent) of the small portion. (*R*)-**14**: colorless oil; $[\alpha]_D$ +33.1° (*c* 0.58, $CHCl_3$); EIMS *m/z* 257 ($M^+ - CH_3$), 215 ($M^+ - C_4H_9$); HREIMS $M^+ - CH_3$ *m/z* obsd 257.1957, $C_{14}H_{29}O_2Si$ required 257.1937; ^1H NMR (400 MHz) δ 0.07 (3H, s), 0.08 (3H, s), 0.88 (3H, t, *J* = 7.1 Hz), 0.92 (9H, s), 3.96 (1H, ddd, *J* = 1.7, 5.6, 7.0 Hz), 9.59 (1H, d, *J* = 1.7 Hz).

(*R*)-*O*-(*tert*-Butyldimethylsilyl)-1,1-dibromodec-1-en-3-ol [(*R*)-15]. To a stirred cold (0 °C) solution of CBr_4 (19.6 g, 59.1 mmol) in dry CH_2Cl_2 (50 mL) was added a solution of triphenylphosphine (31.0 g, 118 mmol) in dry CH_2Cl_2 (50 mL) under an argon atmosphere, and the mixture was stirred for 30 min at 0 °C. After the mixture was cooled to −78 °C, a solution of the above-mentioned crude (*R*)-**14** (5.3 g) in dry CH_2Cl_2 (50 mL) was added. The mixture was then allowed to warm to 0 °C and stirred for 2 h at this temperature. The mixture was diluted with ether and filtered by a fritted glass filter. The filtrate was washed with H_2O, saturated $NaHCO_3$ solution, saturated NH_4Cl solution, and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (hexane as an eluent) to give (*R*)-*O*-(*tert*-butyldimethylsilyl)-1,1-dibromodec-1-en-3-ol [(*R*)-**15**] (6.4 g, 78% yield): colorless oil; $[\alpha]_D$ +3.9° (*c* 1.25, $CHCl_3$); EIMS *m/z* 411, 413, 415 ($M^+ - CH_3$, 1:2:1); HREIMS $M^+ - CH_3$ *m/z* obsd 411.0344, $C_{15}H_{29}OSi^{79}Br_2$ required 411.0354; ^1H NMR (400 MHz) δ 0.07 (3H, s), 0.08 (3H, s), 0.89 (9H, s), 0.89 (3H, t, *J* = 6.9 Hz), 4.28 (1H, td, *J* = 5.5, 8.0 Hz), 6.38 (1H, d, *J* = 8.0 Hz).

(*R*)-*O*-(*tert*-Butyldimethylsilyl)dec-1-yn-3-ol [(*R*)-16]. To a stirred cold (−78 °C) solution of (*R*)-**15** (6.2 g, 14.5 mmol) in dry THF (50 mL) was added a 1.59 M solution of butyllithium in hexane (19.6 mL, 31.1 mmol) under an argon atmosphere. After being stirred for 30 min at −78 °C, the mixture as diluted with ether, washed with saturated NH_4Cl solution, H_2O, and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (hexane:EtOAc = 50:1 as an eluent) to give (*R*)-*O*-(*tert*-butyldimethylsilyl)dec-1-yn-3-ol [(*R*)-**16**] (3.8 g, 99% yield): colorless oil; $[\alpha]_D$ +30.3° (*c* 2.18, $CHCl_3$); EIMS *m/z* 268 (M^+), 253 ($M^+ - CH_3$), 211 ($M^+ - C_4H_9$); HREIMS M^+ *m/z* obsd 268.2225, $C_{16}H_{32}OSi$ required 268.2222; ^1H NMR (400 MHz) δ 0.11 (3H, s), 0.13 (3H, s),0.88 (3H, t, *J* = 6.6 Hz), 0.91 (9H, s), 2.36 (1H, d, *J* = 2.1 Hz), 4.33 (1H, dt, *J* = 2.1, 6.5 Hz).

(*R*)-4-[(*tert*-Butyldimethylsilyl)oxy]undec-2-yn-1-al [(*R*)-17]. To a stirred cold (−78 °C) solution of (*R*)-**16** (1.0 g, 3.73 mmol) in dry THF (25 mL) was added a 1.59 M solution of butyllithium in hexane (2.8 mL, 4.45 mmol) under an argon atmosphere, and the mixture was stirred for 10 min at −78 °C. After addition of boron trifluoride etherate (0.55 mL, 4.45 mmol), the mixture was stirred for 10 min at −78 °C, and then dry DMF (0.58 mL, 7.49 mmol) was added. After being stirred for 10 min at −78 °C, the mixture was diluted with ether, washed with saturated NH_4Cl solution, saturated $NaHCO_3$ solution, H_2O, and saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (eluted with hexane and then hexane:Et_2O = 50:1) to give (*R*)-4-[(*tert*-butyldimethylsilyl)-oxy]undec-2-yn-1-al [(*R*)-**17**] (790 mg, 78% yield): colorless oil; $[\alpha]_D$ +20.8° (*c* 2.25, $CHCl_3$); EIMS *m/z* 281 ($M^+ - CH_3$), 239 ($M^+ - C_4H_9$); HREIMS $M^+ - C_4H_9$ *m/z* obsd 239.1385, $C_{13}H_{23}O_2Si$ required 239.1467; IR (film) 2226, 2204, 1674 cm^{-1}; ^1H NMR (400 MHz) δ 0.12 (3H, s), 0.15 (3H, s), 0.89 (3H, t, *J* = 7.0 Hz), 0.92 (9H, s), 4.52 (1H, t, *J* = 6.5 Hz), 9.24 (1H, s).

(*R*)-*O*-(*tert*-Butyldimethylsilyl)-1,1-dibromododec-1-en-3-yn-5-ol [(*R*)-18]. To a stirred cold (0 °C) solution of CBr_4 (2.2 g, 6.63 mmol) in dry CH_2Cl_2 (15 mL) was added a solution of triphenylphosphine (3.5 g, 13.3 mmol) in dry CH_2Cl_2 (15 mL) under an argon atmosphere, and the mixture was stirred for 30 min at 0 °C. After the solution was cooled to −78 °C, a solution of (*R*)-17 (490 mg, 1.66 mmol) in dry CH_2Cl_2 (15 mL) was added. The mixture was then allowed to warm to 0 °C and stirred for 2 h at this temperature. The mixture was diluted with ether, washed with saturated NH_4Cl solution, H_2O, and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (hexane as an eluent) to give (*R*)-*O*-(*tert*-butyldimethylsilyl)-1,1-dibromodec-1-en-3-yn-5-ol [(*R*)-18] (660 mg, 86% yield): colorless oil; $[\alpha]_D$ +26.5° (*c* 1.75, $CHCl_3$); EIMS *m/z* 435, 437, 439 ($M^+ - CH_3$, 1:2:1); HREIMS $M^+ - CH_3$ *m/z* obsd 437.0286, $C_{17}H_{29}OSi^{79}Br^{81}Br$ required 437.0334; IR (film) 2212 cm^{-1}; ^1H NMR (400 MHz) δ 0.12 (3H, s), 0.14 (3H, s), 0.88 (3H, t, *J* = 7.0 Hz), 0.91 (9H, s), 4.46 (1H, dt, *J* = 1.7, 6.5 Hz), 6.58 (1H, d, *J* = 1.7 Hz).

(*R*)-*O*-(*tert*-Butyldimethylsilyl)dodeca-1,3-diyn-5-ol [(*R*)-19]. To a stirred cold (−78 °C) solution of (*R*)-18 (500 mg, 1.11 mmol) in dry THF (10 mL) was added a 1.59 M solution of butyllithium in hexane (1.46 mL, 2.32 mmol) under an argon atmosphere. After being stirred for 30 min at −78 °C, the mixture was diluted with ether, washed with saturated NH_4Cl solution, H_2O and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (hexane as an eluent) to give (*R*)-*O*-(*tert*-butyldimethylsilyl)dodeca-1,3-diyn-5-ol [(*R*)-19] (292 mg, 90% yield): colorless oil; $[\alpha]_D$ +41.5° (*c* 1.59, $CHCl_3$); CIMS *m/z* 293 ($M^+ + 1$), 277 ($M^+ - CH_3$), 235 ($M^+ - C_4H_9$); HREIMS M^+ *m/z* obsd 292.2258, $C_{18}H_{32}OSi$ required 292.2222; IR (film) 2065 cm^{-1}; ^1H NMR (400 MHz) δ 0.10 (3H, s), 0.14 (3H, s), 0.88 (3H, t, *J* = 7.0 Hz), 0.90 (9H, s), 2.15 (1H, br s), 4.37 (1H, t, *J* = 6.5 Hz).

(*R*)-Dodeca-1,3-diyn-5-ol [(*R*)-20)]. To a stirred solution of (*R*)-19 (287 mg, 0.98 mmol) in THF (20 mL) was added 1.0 M solution of tetrabutylammonium fluoride in THF (1.2 mL, 1.2 mmol), and the mixture was stirred for 30 min at room temperature. The mixture was diluted with ether, washed with H_2O and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (eluted with hexane:Et_2O = 4:1, then 3:1) to give (*R*)-dodeca-1,3-diyn-5-ol [(*R*)-20] (174 mg, 99% yield): colorless oil; $[\alpha]_D$ −6.3° (*c* 0.87, $CHCl_3$); EIMS *m/z* 179 ($M^+ + 1$), 161 ($M^+ + 1 - CH_3$); HREIMS $M^+ + 1$ *m/z* obsd 179.1432, $C_{12}H_{19}O$ required 179.1436; IR (film) 3311, 2065 cm^{-1}; ^1H NMR (400 MHz) δ 0.89 (3H, t, *J* = 7.0 Hz), 2.19 (1H, d, *J* = 0.8 Hz), 4.41 (1H, m).

(*R*)-*O*-Acetyldodeca-1,3-diyn-5-ol [(*R*)-21]. To a stirred solution of (*R*)-20 (160 mg, 0.90 mmol) in dry pyridine (1 mL) was added acetic anhydride (0.5 mL, 5.3 mmol), and the mixture was stirred for 10 h at room temperature. The mixture was concentrated under reduced pressure and the residue purified by silica gel column chromatography (hexane:EtOAc = 10:1 as an eluent) to give (*R*)-*O*-acetyldodeca-1,3-diyn-5-ol [(*R*)-21] (196 mg, 99% yield): colorless oil; $[\alpha]_D$ +96.6° (*c* 0.74, $CHCl_3$); EIMS *m/z* 220 (M^+); HREIMS M^+ *m/z* obsd 220.1436, $C_{14}H_{20}O_2$ required 220.1463; IR (film) 2068, 1745 cm^{-1}; ^1H NMR (400 MHz) δ 0.89 (3H, t, *J* = 7.1 Hz), 2.08 (3H, s), 2.18 (1H, br s), 5.37 (1H, br t, *J* = 6.2 Hz).

(*R*)-*O*-[(*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetyl]-dodeca-1,3-diyn-5-ol [(*R*)-22]. To a stirred solution of (*R*)-20 (6 mg, 0.034 mmol) in dry pyridine (0.8 mL) was sequentially added (*N,N*-dimethylamino)pyridine (0.5 mg, 0.0040 mmol) and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (20 μL, 0.11 mmol), and the mixture was stirred for 12 h at room temperature. The mixture was concentrated under reduced pressure and the residue purified by preparative TLC (silica gel plate, hexane:EtOAc = 50:1 as a development solvent, twice developed) to give (*R*)-*O*-[(*S*)-α-methoxy-α-(trifluoromethyl)-phenylacetyl]dodeca-1,3-diyn-5-ol [(*R*)-22] (11.7 mg, 88% yield): ^1H NMR (400 MHz) δ 0.89 (3H, t, *J* = 7.1 Hz), 2.22 (1H, br s), 3.55 (3H, s), 5.54 (1H, br t, *J* = 6.7 Hz), 7.40–7.55 (5H, m).

(*S*)-1-*O*-Benzylnonane-1,2-diol [(*S*)-11]. The epoxide (*R*)-10[20] (11.5 g) was converted to (*S*)-1-*O*-benzylnonane-1,2-diol [(*S*)-11] (17.5 g, 99% yield) under conditions similar to those for the synthesis of (*R*)-11. (*S*)-11: colorless oil; $[\alpha]_D$ +4.8° (*c* 1.43, $CHCl_3$); HREIMS M^+ *m/z* obsd 250.1923, $C_{16}H_{26}O_2$ required 250.1933; the ^1H NMR spectrum of (*S*)-11 was identical with that of (*R*)-11.

(*S*)-1-*O*-Benzyl-2-*O*-(*tert*-butyldimethylsilyl)nonane-1,2-diol [(*S*)-12]. The compound (*S*)-11 (17.5 g) was converted to (*S*)-1-*O*-benzyl-2-*O*-(*tert*-butyldimethylsilyl)nonane-1,2-diol [(*S*)-12] (25.4 g, 99% yield) under conditions similar to those for the synthesis of (*R*)-12. (*S*)-12: colorless oil; $[\alpha]_D$ +10.9° (*c* 1.22, $CHCl_3$); HREIMS $M^+ - C_4H_9$ *m/z* obsd 307.2055, $C_{18}H_{31}O_2Si$ required 307.2093; the ^1H NMR spectrum of (*S*)-12 was identical with that of (*R*)-12.

(*S*)-2-*O*-(*tert*-Butyldimethylsilyl)nonane-1,2-diol [(*S*)-13]. The compound (*S*)-12 (25.4 g) was converted to (*S*)-2-*O*-(*tert*-butyldimethylsilyl)nonane-1,2-diol [(*S*)-13] (13.6 g, 76% yield) under conditions similar to those for the synthesis of (*R*)-13. (*S*)-13: colorless oil; $[\alpha]_D$ +11.7° (*c* 1.09, $CHCl_3$); HREIMS $M^+ - CH_2OH$ *m/z* obsd 243.2171, $C_{14}H_{31}OSi$ required 243.2144; the ^1H NMR spectrum of (*S*)-13 was identical with that of (*R*)-13.

(*S*)-*O*-(*tert*-Butyldimethylsilyl)-1,1-dibromodec-1-en-3-ol [(*S*)-15]. The compound (*S*)-13 (5.0 g) was converted to (*S*)-*O*-(*tert*-butyldimethylsilyl)-1,1-dibromodec-1-en-3-ol [(*S*)-15]. The compound (*S*)-13 (5.0 g) was converted to (*S*)-*O*-(*tert*-butyldimethylsilyl)-1,1-dibromodec-1-en-3-ol [(*S*)-15] (5.3 g, 68% overall yield) *via* (*S*)-14 under conditions similar to those for the synthesis of (*R*)-15. (*S*)-15: colorless oil; $[\alpha]_D$ −2.7° (*c* 1.07, $CHCl_3$); HREIMS $M^+ - CH_2OH$ *m/z* obsd 426.0556, $C_{16}H_{32}OSi^{79}Br_2$ required 426.0589; the ^1H NMR spectrum of (*S*)-15 was identical with that of (*R*)-15.

(*S*)-*O*-(*tert*-Butyldimethylsilyl)dec-1-yn-3-ol [(*S*)-16]. The compound (*S*)-15 (5.3 g) was converted to (*S*)-*O*-(*tert*-butyldimethylsilyl)dec-1-yn-3-ol [(*S*)-16] (2.9 g, 88% yield) under conditions similar to those for the synthesis of (*R*)-16. (*S*)-16: colorless oil; $[\alpha]_D$ −35.5° (*c* 1.13, $CHCl_3$); HREIMS M^+ *m/z* obsd 268.2223, $C_{16}H_{32}OSi$ required 268.2222; the ^1H NMR spectrum of (*S*)-16 was identical with that of (*R*)-16.

(*S*)-4-[(*tert*-Butyldimethylsilyl)oxy]undec-2-yn-1-al [(*S*)-17]. The compound (*S*)-16 (2.9 g) was converted to (*S*)-4-[(*tert*-butyldimethylsilyl)oxy]undec-2-yn-1-al [(*S*)-17] (1.9 g, 58% yield) under conditions similar to those for the synthesis of (*R*)-17. (*S*)-17: colorless oil; $[\alpha]_D$ −45.0° (*c* 0.17, $CHCl_3$); HREIMS M^+ *m/z* obsd 296.2158, $C_{17}H_{32}O_2Si$ required 296.2172; the ^1H NMR spectrum of (*S*)-17 was identical with that of (*R*)-17.

(*S*)-*O*-(*tert*-Butyldimethylsilyl)-1,1-dibromododec-1-en-3-yn-5-ol [(*S*)-18]. The compound (*S*)-17 (1.9 g) was converted to (*S*)-*O*-(*tert*-butyldimethylsilyl)-1,1-dibromododec-1-ene-3-yn-5-ol [(*S*)-18] (2.8 g, 99% yield) under conditions similar to those for the synthesis of (*R*)-18. (*S*)-18: colorless oil; $[\alpha]_D$ −33.1° (*c* 0.74, $CHCl_3$); HREIMS $M^+ - CH_3$ *m/z* obsd 435.0381, $C_{17}H_{29}OSi^{79}Br_2$ required 435.0354; the ^1H NMR spectrum of (*S*)-18 was identical with that of (*R*)-18.

(*S*)-*O*-(*tert*-Butyldimethylsilyl)dodeca-1,3-diyn-5-ol [(*S*)-19]. The compound (*S*)-18 (2.8 g) was converted to (*S*)-*O*-(*tert*-butyldimethylsilyl)dodeca-1,3-diyn-5-ol [(*S*)-19] (1.4 g, 77% yield) under conditions similar to those for the synthesis of (*R*)-19. (*S*)-19: colorless oil; $[\alpha]_D$ −43.4° (*c* 0.80, $CHCl_3$); HREIMS M^+ *m/z* obsd 292.2225, $C_{18}H_{32}OSi$ required 292.2222; the ^1H NMR spectrum of (*S*)-19 was identical with that of (*R*)-19.

(*S*)-Dodeca-1,3-diyn-5-ol [(*S*)-20]. The compound (*S*)-19 (1.4 g) was converted to (*S*)-dodeca-1,3-diyn-5-ol [(*S*)-20] (865 mg, 99% yield) under conditions similar to those for the synthesis of (*R*)-20. (*S*)-20: colorless oil; $[\alpha]_D$ +8.4° (*c* 0.54, $CHCl_3$); HREIMS $M^+ - H_2O$ *m/z* obsd 160.1258, $C_{12}H_{16}$ required 160.1252; the ^1H NMR spectrum of (*S*)-20 was identical with that of (*R*)-20.

(*S*)-*O*-Acetyldodeca-1,3-diyn-5-ol [(*S*)-21]. The compound (*S*)-20 (865 mg) was converted to (*S*)-*O*-acetyldodeca-1,3-diyn-5-ol [(*S*)-21] (1.0 g, 93% yield) under conditions similar to those for the synthesis of (*R*)-21. (*S*)-21: colorless oil; $[\alpha]_D$ −127.8° (*c* 0.66, $CHCl_3$); HREIMS M^+ *m/z* obsd 220.1436, $C_{14}H_{20}O_2$ required 220.1463; the ^1H NMR spectrum of (*S*)-21 was identical with that of (*R*)-21.

(*S*)-*O*-[(*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetyl]-dodeca-1,3-diyn-5-ol [(*S*)-22]. The compound (*S*)-20 (11 mg)

was converted to (*S*)-*O*-[(*S*)-α-methoxy-α-(trifluoromethyl)-phenylacetyl]dodeca-1,3-diyn-5-ol [(*S*)-22] (18.8 mg, 77% yield) under conditions similar to those for the synthesis of (*R*)-22. (*S*)-22: colorless oil; ^{1}H NMR (400 MHz) δ 0.88 (3H, t, *J* = 7.1 Hz), 2.24 (1H, br s), 3.59 (3H, s), 5.58 (1H, t, *J* = 6.7 Hz), 7.4–7.55 (5H, m).

(*R*)-3-[[1-[(*R,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]-oxy]propane-1,2-diol Triacetate [(7*R*,2′*R*)-23, Petrosyne Ia Triacetate]. To a solution of bromovinyl ether (*R*)-9 (45 mg, 0.16 mmol) and acetate (*R*)-21 (35 mg, 0.16 mmol) in dry DMF (3 mL) were sequentially added copper(I) iodide (15 mg, 0.080 mmol), butylamine (0.16 mL, 1.62 mmol), and tetrakis(triphenylphosphine)palladium(0) (92 mg, 0.080 mmol) at room temperature under an argon atmosphere. After being stirred for 3 h at room temperature under an interception of light, saturated $NaHCO_3$ solution was added, and the mixture was extracted with ether. The ethereal solution was washed with saturated $NaHCO_3$ solution, H_2O, and then saturated NaCl solution, dried over anhyd $MgSO_4$, and concentrated under reduced pressure. The residue obtained was chromatographed on a silica gel column (hexane:EtOAc = 3:1 as an eluent) to give (*R*)-3-[[1-[(*R,Z*)-7-hydroxytetradec-1-ene-3,5-diynyl]oxy]propane-1,2-diol triacetate [(7*R*,2′*R*)-23, petrosyne Ia triacetate] (18.3 mg, 27% yield): colorless oil; $[\alpha]_D$ +80.1° (*c* 0.79, MeOH); EIMS *m/z* 420 (M^+), 159 ($M^+ - C_6H_{13}$): HREIMS M^+ *m/z* obsd 420.2152, $C_{23}H_{32}O_7$ required 420.2148; IR (film) 2231, 2142, 1747 cm^{-1}; UV (EtOH, log ε) 292 (4.26), 276 (4.19), 262 (4.19), 250 (3.94), 223 (4.60) nm; ^{1}H NMR (500 MHz) see Table I; ^{13}C NMR (125 MHz) δ 14.0 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 22.6 (CH_2), 25.0 (CH_2), 29.0 (CH_2 × 2), 31.7 (CH_2), 34.6 (CH_2), 62.0 (CH_2), 64.5 (CH_2), 69.8 (CH), 70.2 (C), 71.5 (CH), 73.4 (C), 76.8 (C), 79.7 (C), 85.2 (CH), 158.4 (CH), 169.8 (C), 170.0 (C), 170.5 (C).

(*S*)-3-[[1-[(*R,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]-oxy]propane-1,2-diol Triacetate [(7*R*,2′*S*)-23)]. Coupling reaction of bromovinyl ether (*S*)-9 (41 mg) and acetate (*R*)-21 (32 mg) under conditions similar to those for the synthesis of (7*R*,2′*R*)-23 gave (*S*)-3-[[1-[(*R,Z*)-7-hydroxytetradec-1-ene-3,5-diynyl]]-oxy]propane-1,2-diol triacetate [(7*R*,2′*S*)-23] (9.6 mg, 16% yield): colorless oil; $[\alpha]_D$ +114.0° (*c* 0.93, MeOH); HREIMS M^+ *m/z* obsd 420.2123, $C_{23}H_{32}O_7$ required 420.2148; IR (film) 2231, 2142, 1747 cm^{-1}; UV (EtOH, log ε) 292 (4.27), 276 (4.37), 262 (4.20), 250 (3.97), 223 (4.62) nm; each ^{1}H- NMR (500 MHz) (Table I) and ^{13}C-NMR (125 MHz) spectrum of (7*R*,2′*S*)-23 was superimposable upon that of (7*R*,2′*R*)-23, respectively.

(*R*)-3-[1-[[(*S,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]-oxy]propane-1,2-diol Triacetate [(7*S*,2′*R*)-23, Petrosyne Ib Triacetate]. Coupling reaction of bromovinyl ether (*R*)-9 (93 mg) and acetate (*S*)-21 (73 mg) under conditions similar to those for the synthesis of (7*R*,2′*R*)-23 gave (*R*)-3-[[1-[(*S,Z*)-7-hydroxytetradec-1-ene-3,5-diynyl]]oxy]propane-1,2-diol triacetate [(7*S*,2′*R*)-23, petrosyne Ib triacetate] (15.2 mg, 11% yield): colorless oil; $[\alpha]_D$ −94.5° (*c* 0.54, MeOH); HREIMS M^+ *m/z* obsd 420.2129, $C_{23}H_{32}O_7$ required 420.2148; the spectral data of (7*S*,2′*R*)-23 were identical with those of (7*R*,2′*S*)-23.

(*S*)-3-[[1-[(*S,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]oxy]-propane-1,2-diol Triacetate [(7*S*,2′*S*)-23]. Coupling reaction of bromovinyl ether (*S*)-9 (100 mg) and acetate (*S*)-21 (78 mg) under conditions similar to those for the synthesis of (7*R*,2′*R*)-23 gave (*S*)-3-[[1-[(*S,Z*)-7-hydroxytetradec-1-ene-3,5-diynyl]]oxy]-propane-1,2-diol triacetate [(7*S*,2′*S*)-23] (43.6 mg, 30% yield): colorless oil; $[\alpha]_D$ −42.8° (*c* 2.00, MeOH); HREIMS M^+ *m/z* obsd 420.2135, $C_{23}H_{32}O_7$ required 420.2148; the spectral data of (7*S*,2′*S*)-23 were identical with those of (7*R*,2′*R*)-23.

(*S*)-3-[[1-[(*R,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]-oxy]propane-1,2-diol [(7*R*,2′*S*)-24, Petrosyne Ia]. To a solution of triacetate (7*R*,2′*R*)-23 (7 mg, 0.017 mmol) in MeOH (1 mL) was added Li_2CO_3 (2 mg, 0.027 mmol), and the mixture was stirred for 5 h at room temperature. The mixture was diluted with ether and filtered through a short silica gel column. The eluate was concentrated under reduced pressure, and the residue obtained was purified by silica gel column chromatography followed by normal-phase HPLC (hexane:EtOAc = 1:2 as an eluent) to give (*S*)-3-[[1-[(*R,Z*)-7-hydroxytetradec-1-ene-3,5-diynyl]]oxy]-propane-1,2-diol [(7*R*,2′*S*)-24, petrosyne Ia] (4.9 mg, 99% yield): colorless oil; $[\alpha]_D$ +5.9° (*c* 0.5, MeOH); EIMS *m/z* 294 (M^+); HREIMS M^+ *m/z* obsd 294.1892, $C_{17}H_{26}O_4$ required 294.1831; IR (film) 3355, 2229, 2145 cm^{-1}; UV (EtOH, log ε) 292 (4.02), 276 (4.10), 262 (3.94), 250 (3.69), 223 (432) nm; ^{1}H NMR (500 MHz) see Table I; ^{13}C NMR (125 MHz) δ 14.1 (CH_3), 22.6 (CH_2), 25.1 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 37.6 (CH_2), 63.1 (CH), 63.2 (CH_2), 69.8 (C), 70.4 (CH), 73.6 (C), 75.0 (CH_2), 76.9 (C), 83.6 (C), 84.7 (CH), 159.1 (CH).

(*R*)-3-[[1-[(*R,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]-oxy]propane-1,2-diol [(7*R*,2′*R*)-24]. Triacetate (7*R*,2′*S*)-23 (5 mg) was converted to triol (7*R*,2′*R*)-24 (3.5 mg, 99% yield) under conditions similar to those for the preparation of (7*R*,2′*S*)-24. (7*R*,2′*R*)-24: colorless oil; $[\alpha]_D$ −6.8° (*c* 0.44, MeOH); HREIMS M^+ *m/z* obsd 294.1847, $C_{17}H_{26}O_4$ required 294.1831; each ^{1}H NMR (500 MHz) (Table I) and ^{13}C NMR (125 MHz) spectrum of (7*R*,2′*R*)-24 was superimposable upon that of (7*R*,2′*S*)-24, respectively.

(*S*)-3-[[1-[(*S,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]oxy]-propane-1,2-diol [(7*S*,2′*S*)-24, Petrosyne Ib]. Triacetate (7*S*,2′*R*)-23 (6.4 mg) was converted to triol (7*S*,2′*S*)-24 (4.2 mg, 93% yield) under conditions similar to those for the preparation of (7*R*,2′*S*)-24. (7*S*,2′*S*)-24: colorless oil; $[\alpha]_D$ +7.2° (*c* 0.21, MeOH); HREIMS M^+ *m/z* obsd 294.1848, $C_{17}H_{26}O_4$ required 294.1831; the spectral data of (7*S*,2′*S*)-24 were identical with those of (7*R*,2′*R*)-24.

(*R*)-3-[1-[(*S,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]oxy]-propane-1,2-diol [(7*S*,2′*R*)-24]. Triacetate (7*S*,2′*S*)-23 (12.5 mg) was converted to triol (7*S*,2′*R*)-24 (8.7 mg, 99% yield) under conditions similar to those for the preparation of (7*R*,2′*S*)-24. (7*S*,2′*R*)-24: colorless oil; $[\alpha]_D$ −0.8° (*c* 0.5, MeOH); HREIMS M^+ *m/z* obsd 294.1837, $C_{17}H_{26}O_4$ required 294.1831; the spectral data of (7*S*,2′*R*)-24 were identical with those of (7*R*,2′*S*)-24.

(*R*)-3-[[1-[(*R,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]-oxy]propane-1,2-diol Tris-(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate [(7*R*,2′*R*)-25]. To a solution of triol (7*R*,2′*S*)-24 (4.8 mg, 0.016 mmol) in dry pyridine (0.5 mL) were added (*N,N*-dimethylamino)pyridine (1 mg, 0.008 mmol) and (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (20 μL, 0.11 mmol), and the mixture was stirred for 12 h at room temperature. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane:EtOAc = 3:1 as an eluent) to give MTPA ester (7*R*,2′*R*)-25 (9.9 mg, 64% yield): colorless oil; $[\alpha]_D$ +58.0° (*c* 0.4, MeOH); EIMS *m/z* 942 (M^+); IR (film) 2232, 2144, 1757 cm^{-1}; UV (EtOH, log ε) 292 (4.13), 276 (4.21), 267 (4.09), 262 (4.10), 250 (3.88), 223 (4.51) nm; ^{1}H NMR (400 MHz) see Table II.

(*S*)-3-[[1-[(*R,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]-oxy]propane-1,2-diol Tris-(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate [(7*R*,2′*S*)-25]. Triol (7*R*,2′*R*)-24 (4.4 mg) was converted to MTPA ester (7*R*,2′*S*)-25 (8.0 mg, 57% yield) under conditions similar to those for the preparation of (7*R*,2′*R*)-25. (7*R*,2′*S*)-25: colorless oil; $[\alpha]_D$ +18.3° (*c* 0.4, MeOH); EIMS *m/z* 942 (M^+); IR (film) 2232, 2144, 1757 cm^{-1}; UV (EtOH, log ε) 292 (4.14), 276 (4.21), 267 (4.09), 262 (4.10), 250 (3.89), 223 (4.51) nm; ^{1}H NMR (400 MHz) see Table II.

(*R*)-3-[[1-[(*S,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]oxy]-propane-1,2-diol Tris-(*R*)-α-methoxy-α-(trifluoromethyl)-phenylacetate [(7*S*,2′*R*)-25]. Triol (7*S*,2′*S*)-24 (1.6 mg) was converted to MTPA ester (7*S*,2′*R*)-25 (2.1 mg, 41% yield) under conditions similar to those for the preparation of (7*R*,2′*R*)-25. (7*S*,2′*R*)-25: colorless oil; $[\alpha]_D$ +44.7° (*c* 0.21, MeOH); EIMS *m/z* 942 (M^+); IR (film) 2232, 1757 cm^{-1}; UV (EtOH, log ε) 292 (3.96), 276 (4.04), 267 (3.91), 262 (3.93), 250 (3.71), 223 (4.37) nm; ^{1}H NMR (400 MHz) see Table II.

(*S*)-3-[[1-[(*S,Z*)-7-Hydroxytetradec-1-ene-3,5-diynyl]]oxy]-propane-1,2-diol Tris-(*R*)-α-methoxy-α-(trifluoromethyl)-phenylacetate [(7*S*,2′*S*)-25]. Triol (7*S*,2′*R*)-24 (3.5 mg) was converted to MTPA ester (7*S*,2′*S*)-25 (5.0 mg, 45% yield) under conditions similar to those for the preparation of (7*R*,2′*R*)-25. (7*S*,2′*S*)-25: colorless oil; $[\alpha]_D$ +13.7° (*c* 0.50, MeOH); EIMS *m/z* 942 (M^+); IR (film) 2232, 1757 cm^{-1}; UV (EtOH, log ε) 292 (4.11), 276 (4.20), 267 (4.07), 262 (4.07), 250 (3.81), 223 (4.49) nm; ^{1}H NMR (400 MHz) see Table II.

Conversion of Triacetate 2 into MTPA Esters. Triacetate 2 (1 mg, 0.0024 mmol) in MeOH (0.5 mL) was treated with Li_2CO_3 (1 mg, 0.014 mmol) under conditions similar to those for the

preparation of (7*R*,2'*S*)-**24** to give a crude alcohol which was used for the next acylation without any purification.

The crude alcohol in dry pyridine (250 μL) was treated with (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (10 μL, 0.05 mmol) in the presence of (*N*,*N*-dimethylamino)pyridine (0.5 mg, 0.004 mmol). The workup similar to that for the preparation of the MTPA ester (7*R*,2'*R*)-**25** gave a mixture of products, which was subjected to silica gel column chromatography followed by HPLC purification (silica gel, hexane:EtOAc = 3:1 as an eluent, UV 254 nm) to give a mixture (0.5 mg) of (7*R*,2'*R*)-**25** and (7*S*,2'*R*)-**25** in a ratio of about 1:1. ^{1}H NMR (400 MHz) see Table II. Further separation of this mixture by HPLC failed.

Conversion of Triacetate 4 into MTPA Esters. Triacetate **4** (1 mg) was treated with Li_2CO_3 followed by treatment with (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride under conditions similar to those for the conversion of triacetate **2**, giving a mixture of the MTPA ester (7*R*,2'*R*)-**26** and (7*S*,2'*R*)-**26**, in a ratio of about 1:1: colorless oil; ^{1}H NMR (400 MHz) δ 0.85 (6H, d, *J* = 6.6 Hz), 0.86 (6H, d, *J* = 6.6 Hz), 3.42 (6H, s), 3.49 (6H, s), 3.53 (3H, s), 3.58 (3H, s), 3.96 (2H, dd, *J* = 4.7, 12.1 Hz), 4.41 (2H, dd, *J* = 5.3, 12.4 Hz), 4.48 (1H, d, *J* = 6.4 Hz), 4.49 (1H, d, *J* = 6.4 Hz), 4.78 (2H, dd, *J* = 3.3, 12.4 Hz), 5.49 (2H, m), 5.60 (1H, t, *J* = 6.0 Hz), 5.63 (1H, t, *J* = 6.0 Hz), 6.09 (1H, d, *J* = 6.4 Hz), 6.10 (1H, d, *J* = 6.4 Hz), 7.35–7.60 (30H, m).

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Supplementary Material Available: ^{1}H NMR spectra of **2** and **4** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.