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Structure and Absolute Configuration of Sargatriol, a New Isoprenoid Chromenol from a Brown Alga, *Sargassum tortile* C. AGARDH[1)]

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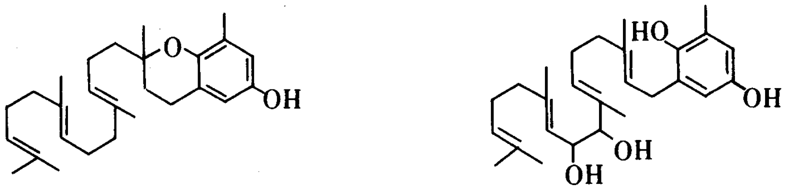
The structure of sargatriol, a new phenolic compound containing an oxygenated isoprenoid component isolated from a brown alga *Sargassum tortile*, was elucidated to be **3** on the basis of spectral and chemical evidence. The absolute stereochemistry was established from the circular dichroism (CD) of sargatriol (**3**) and the shift reagent-induced CD of the methyl ether (**4**).

Keywords——*Sargassum tortile*; marine brown alga; sargatriol; oxygenated isoprenoid chromenol; ^{1}H-NMR; spin decoupling experiment; shift reagent-induced CD

Members of the brown algae genus *Sargassum*, family Sargassaceae, have antibiotic activity[2)] and a promoting effect on the larval settlement of epiphytic hydrozoa.[3)] In Japan studies on the metabolites of *Sargassum* species have led to the isolation of δ-tocotrienol (**1**) and its epoxide,[4)] which are attractants of swimming larvae of a symbiotic hydrozoan *Coryne uchidai*, as well as sargatetraol (**2**) and geranylgeranylbenzoquinone intermediates.[5)] In another study on this interesting group of algae, Nakazawa *et al.* reported that *S. tortile* C. AGARDH (Yoremoku in Japanese) has antitumor activity,[6)] which prompted us to investigate the metabolites of this alga.

In a preliminary communication,[1)] we reported the isolation of a tocopherol-like compound, sargatriol, from *S. tortile*, for which we proposed the structure **3** based on chemical and spectroscopic analyses. The present paper deals with the detailed structural study of sargatriol, including the absolute stereochemistry.

Air-dried seaweed, *S. tortile*, collected at Wakasa Bay, Fukui Prefecture, was extracted with ether. The neutral fraction of the ether extract was chromatographed on silica gel and then subjected to repeated preparative thin layer chromatography (TLC) to afford sargatriol as a pale yellow oil.



1 **2**

Chart 1

Sargatriol (**3**), $[\alpha]_D^{21}$ +16.0° (c=1.0, $CHCl_3$), showed a molecular ion peak at m/z 426 ($C_{27}H_{38}O_4$) in the mass spectrum (MS) and a strong hydroxyl band at 3400 cm^{-1} in the infrared (IR) spectrum. The nuclear magnetic resonance (NMR) spectrum of **3** showed signals at δ 1.33 (3H, *tert*-CH_3), 1.58, 1.65 (each 6H, four vinyl CH_3), 2.10 (3H, toluene CH_3), 3.80 (1H, d, J=8 Hz, >CHOH), 4.30 (1H, dd, J=8 and 8.5 Hz, >CHOH), 5.53, 6.25 (each 1H, pair of d, J=10 Hz, olefinic protons), 4.9—5.6 (3H, olefinic protons), 6.32 and 6.48 (each 1H, pair of d, J=2.5 Hz, aromatic protons). Its ultraviolet (UV) spectrum exhibited an absorption maximum at 335 nm (ϵ 2560) which shifted to 355 nm on addition of ethanolic potassium hydroxide. Further, treatment of **3** with diazomethane afforded a methyl ether (**4**), NMR δ 3.72 (3H, OCH_3), and an unexpected carbamate (**5**) as a by-product.[7] These data indicate the presence of a phenolic styrene chromophore.[8]

Acetylation of **3** with acetic anhydride in pyridine gave an oily triacetate (**6**) $[\alpha]_D^{19}$ +34.1° (c=1.0, $CHCl_3$), whose molecular formula $C_{33}H_{44}O_7$ was confirmed by the high resolution MS. Lithium aluminum hydride reduction of the triacetate (**6**) regenerated sargatriol (**3**).

The UV spectrum of **6** exhibited characteristic absorptions at 228, 267, 277, and 320 nm (ϵ 34780, 5520, 4420, and 3310, respectively), indicating the presence of a 6-chromenol moiety.[8] The IR spectrum of **6** showed strong absorptions of acetoxyl groups at 1735 and 1235 cm^{-1} and the NMR spectrum (Fig. 1) "showed" signals due to the three newly introduced acetyl groups at δ 1.99, 2.03 (carbinol acetates), and 2.24 (phenolic acetate) and those due to hydrogens geminal to the acetoxyl groups at δ 5.18 (d, J=8 Hz) and 5.72 (dd, J=9.5 and 8 Hz), along with other signals.

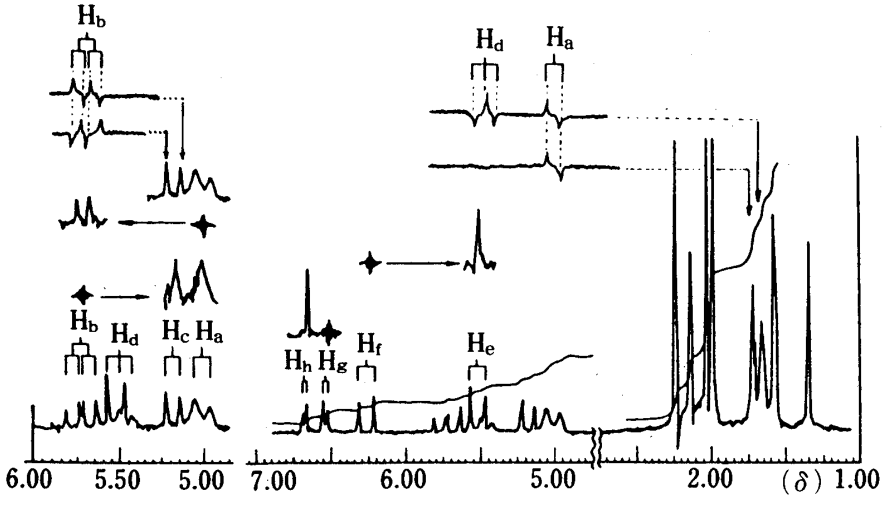
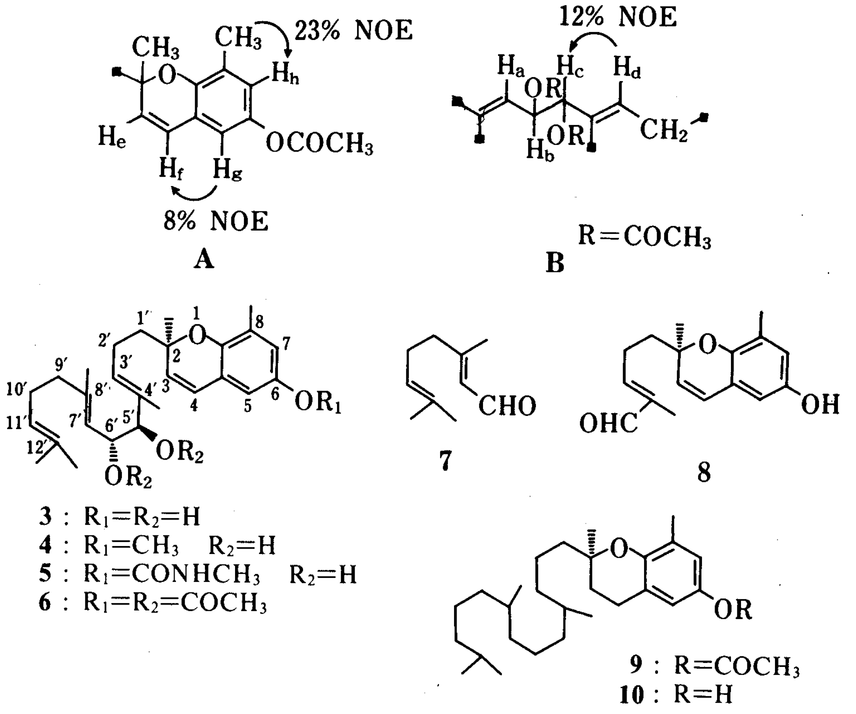


Fig. 1. ^{1}H NMR, NMDR, and INDOR Spectra of Sargatriol Triacetate (**6**) (100 MHz)

Nuclear magnetic double resonance (NMDR) experiments involving a recently developed INDOR technique[9] were carried out in order to elucidate the hydrogen sequences in the acetate (**6**). The INDOR and NMDR experiments between the signals at δ 6.67 and 6.54 and between those at δ 6.26 and 5.52 revealed that these can be assigned to aromatic *meta*-coupled hydrogens (H_h and H_g, J=2.5 Hz) and *cis*-oriented olefinic hydrogens (H_f and H_e, J=10 Hz), respectively. Irradiation of the toluene methyl signal at δ 2.14 gave a 23% nuclear Overhauser effect (NOE) increase in the signal at δ 6.67 (H_h) and no increase in that at δ 6.54 (H_g). Moreover, an 8% NOE increase in the signal intensity at δ 6.26 (H_f) was seen upon irradiation at δ 6.54 (H_g). Consideration of these results and the UV data of **6** indicates the presence of the 8-methyl-6-chromenol moiety (**A**) in sargatriol triacetate (**6**).

On the other hand, irradiation of the quartet at δ 5.72 (H_b) collapsed both the doublet at δ 5.05 (olefinic proton H_a) and the doublet at δ 5.18 (H_c) to singlets. In turn, irradiation at δ

5.05 transformed the quartet at δ 5.72 into a doublet. Also, a 12% NOE increase in the signal at δ 5.18 was seen upon irradiation of the triplet at δ 5.50 attributable to an olefinic proton (H_d). From these observations, the presence of the partial structure (**B**) can be posturated, as in **6** (Chart 2).



A **B**

3 : $R_1=R_2=H$
4 : $R_1=CH_3$ $R_2=H$
5 : $R_1=CONHCH_3$ $R_2=H$
6 : $R_1=R_2=COCH_3$

7 **8**

9 : $R=COCH_3$
10 : $R=H$

Chart 2

Then, oxidative cleavage of the α-gylcol system in **3** was undertaken. Treatment of **3** with periodic acid in aqueous dioxane followed by TLC separation of the products gave two conjugated aldehydes. The less polar product (**7**), a colorless oil, showed the molecular ion peak at m/z 152 ($C_{10}H_{16}O$), and eventually it was identified as geranial (citral-a)[10] by direct IR, NMR, and gas chromatography-mass spectrometric (GC–MS) comparisons with an authentic sample.

On the other hand, though the more polar product (**8**) was unstable and could not be isolated in a pure state, it showed IR bands at 2730 and 1670 cm^{-1} (α,β-unsaturated aldehyde) and NMR signals due to an aldehyde proton (δ 9.42, s), an olefinic proton (δ 5.95, m) and a vinyl methyl (δ 1.65, br) together with signals arising from the partial structure **A**. The mass spectrum of **8** gave the molecular ion peak at m/z 272 ($C_{17}H_{20}O_3$) and the base peak at m/z 175 (b in Chart 3), which is characteristic of chromenol derivatives[11] (*vide infra*). Therefore, the structure of this product can be represented by the formula **8**.

Combination of the two aldehydes (**7**) and (**8**) can give only the structure (**3**) with two hydroxyl groups at C(5′) and C(6′) for sargatriol. This conclusion was supported by its mass spectrum, which showed three intense peaks at m/z 273, 175 (base peak), and 69. With the triacetate (**6**), the corresponding peaks were observed at m/z 315, 217 (base peak), and 69, and their compositions were determined to be $C_{19}H_{23}O_4$ (Calcd: 315.1596; Found: 315.1615), $C_{13}H_{13}O_3$ (Calcd: 217.0865; Found: 217.0893), and C_5H_9 (Calcd: 69.0704; Found: 69.0705), respectively, by high resolution MS. As a consequence, these peaks are ascribed to the fragment ions a, b, and c, respectively.[11]

The molecular framework of sargatriol (**3**) was, finally, confirmed by the following experiments. Catalytic reduction of the triacetate (**6**) over Pd-C caused the hydrogenolytic elimination of two acetoxyl groups accompanied with the hydrogenation of the double bonds, giving a

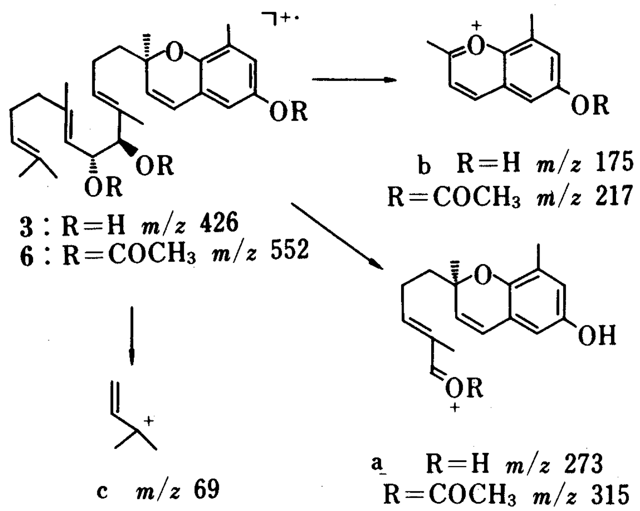


Chart 3

saturated phenol acetate (**9**) with the composition $C_{29}H_{48}O_3$ (M^+, Calcd: 444.3603; Found: 444.3554). Hydrolysis of this acetate with dil. HCl in methanol gave an oily phenol (**10**). The IR and NMR spectra of **10** were identical with those of the hexahydro compound of δ-tocotrienol (**1**).[4]

Next, we investigated the circular dichroism (CD) of sargatriol in order to determine the stereochemistry unambiguously. Crabbé has already performed an extensive study on the CD and optical rotatory dispersion (ORD) of chiral molecules with a stylene chromophore.[12] Thus, a strong nagative Cotton effect associated with the 260—270 nm transition indicates that the double bond and the benzene ring of the styrene chromophore are twisted in the form of a right-handed helix. Conversely, an intense positive Cotton effect is indicative of a left-handed helix.

The CD curve of sargatriol (**3**) displayed a negative Cotton effect in the 265—275 nm region due to the styrene chromophore, as shown in Fig. 2, indicating that the chromenol ring has a positive chirality. The bulky isoprenoid side chain of **3** preferentially adopts the pseudoequatorial conformation and thus the absolute configuration at C(2) was determined to be "*R*". This stereochemical assignment is in good accordance with those of naturally occurring tocopheroles, all of which have a (2*R*)-chromanol ring.[13]

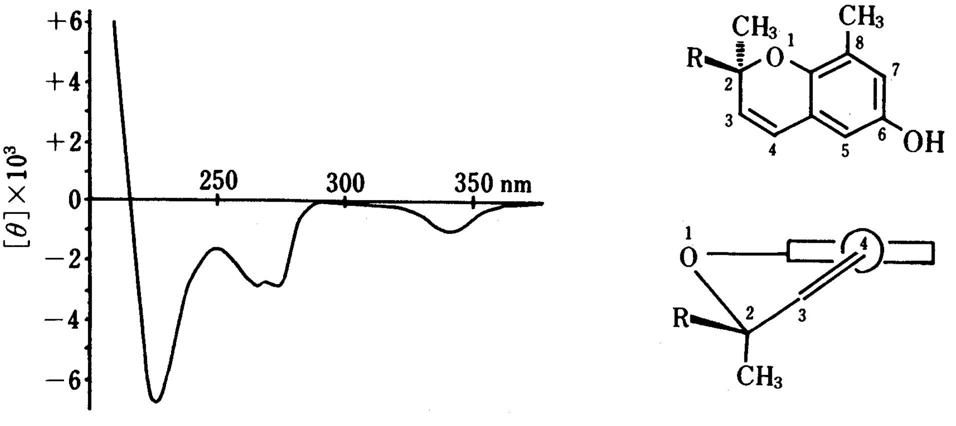
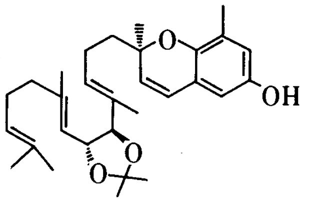


Fig. 2. CD Spectrum of 2.97×10^{-4} M Sargatriol (**3**) in Methanol

$[\theta]_{375}$ 0, $[\theta]_{335}$ −1060, $[\theta]_{287}$ 0, $[\theta]_{274.5}$ −2660, $[\theta]_{265}$ −2660, $[\theta]_{250}$ −1330, $[\theta]_{228}$ −6880, $[\theta]_{218}$ 0, $[\theta]_{210}$ +28000.

Another stereochemical problem is the configuration of the acyclic α-glycol moiety in the isoprenoid side chain of sargatriol. Recently, Nakanishi *et al.*[14] have demonstrated that the induced CD obtained by using nickel acetylacetonate [$Ni(acac)_2$] in conjunction with tris(dipivaloylmethanato)praseodymium [Pr(dpm)$_3$] offers a general method for determining the absolute configuration of various glycols and amino alcohols, acyclic as well as cyclic. Application of this method in our case, however, is limited to *threo*-type α-glycols which can form fairly stable Ni- or Pr-glycol complexes having both of the bulky groups in *trans* pseudoequatorial orientations.[15]

In order to establish the relative configuration of the α-glycol system, sargatriol (**3**) was converted to an acetonide derivative. Heating of **3** in 2,2-dimethoxypropane with a catalytic amount of *p*-toluenesulfonic acid (TsOH) afforded the acetonide (**11**), which upon treatment with TsOH in methanol gave **3**, indicating that no stereochemical change occurred during the reaction. The NMR spectrum of **11** showed two signals at δ 3.97 (d, J=8.5 Hz) and δ 4.47 (t, J=8.5 Hz) attributable to protons geminal to the acetonide oxygens. The coupling constant (8.5 Hz) of these protons suggests that two substituents on the 1,3-dioxolane ring are in *trans*-configuration.[16] This was confirmed by NOE measurements[17] as follows: +11% and +5% NOE's were observed between C(3′)-H (δ 5.50) and C(5′)-H (δ 3.97) and between C(5′)-H and C(7′)-H (δ 5.17), respectively, and also +25% and +18% NOE's were detected between C(4′)-CH$_3$ (δ 1.64) and C(6′)-H (δ 4.47) and between C(8′)-CH$_3$ (δ 1.59) and C(6′)-H, respectively. On the other hand, no NOE's were observed between C(5′)-H and C(6′)-H and between C(6′)-H and C(7′)-H. The above results require the *trans*-configuration of C(5′)-H and C(6′)-H in the acetonide (**11**). Thus, the shift reagent-induced CD method is applicable to the triol (**3**).



11

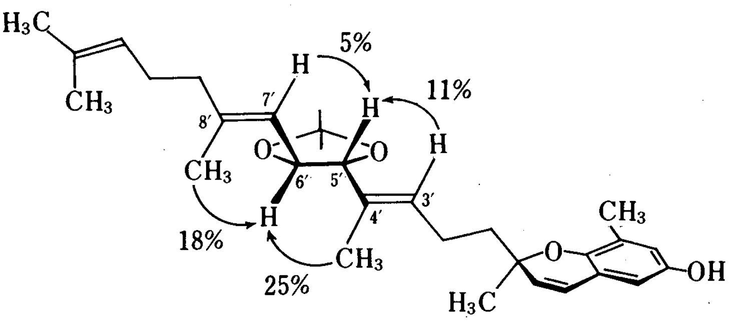
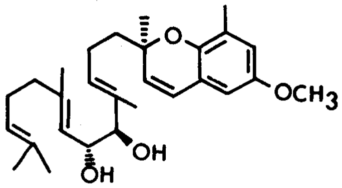


Chart 4

It is appropriate to mention here that the signs of Cotton effects obtained from induced CD curves depend on both the metal reagents used and the substitution patterns of acyclic α-glycols.[14] Therefore, we compared the induced CD Cotton effects of sargatriol methyl ether (**4**), under the same conditions, with those of dimethyl (+)-tartarate (**12**) which has known absolute stereochemistry. In the presence of metal reagents,two carbomethoxyl groups of **12** should adopt pseudoequatorial conformation, giving a positive chirality of its glycol system, which is defined as clockwise rotation from one hydroxyl group to the other in the Newman projection.

As shown in Table I, the methyl ether (**4**) displayed reversed Cotton effects with respect to those of **12**. Since the chromenol chromophore of **4** is far from the glycolic asymmetric center and the interaction between them should be negligible, it is reasonable to consider that the electronic transitions in **4** and **12** are essentially equivalent. Accordingly the stereochemistry at C(5′) and C(6′) in **4** was determined to be (5′*R*, 6′*R*).

TABLE I. Shift Reagent-induced Cotton Effects of Sargatriol Methyl Ether (**4**) and Dimethyl Tartarate (**12**) (in CCl_4)



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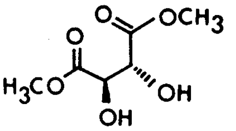

12

	Ni $(acac)_2$		Pr $(dpm)_3$	
	nm	$\Delta\epsilon$	nm	$\Delta\epsilon$
4	314	$+1.78$	317	-0.28
	287	-0.52	299	$+1.39$
12	318	-1.79	314	$+2.33$
	290	$+0.73$	290	-1.18

Substrate concentration was *ca.* 3.5×10^{-4}M.
Molar ratio of substrate to reagent was 1:1.

From the results described above, the structure of sargatriol was established as **3**, including the absolute stereochemisry.

An interesting feature of sargatriol (**3**) as well as sargatetraol (**2**) is that hydroxylation occurs at an inner position of their isoprenoid side chains. The biosynthetic derivation of these metabolites is a matter for conjecture, but it seems likely that they may arise from geranylgeranylbenzoquinones[5c)] which have recently been isolated from the same alga.

Experimental

Unless otherwise stated, IR spectra were measured in $CHCl_3$, and UV spectra in 95% ethanol. NMR spectra were taken in $CDCl_3$ with tetramethylsilane as the internal reference on Varian A-60 or HA-100D instruments. Mass spectra and high resolution mass spectra were determined on a Hitachi RMU-6D mass spectrometer using a direct inlet system and on a JEOL-01SG double-focusing mass spectrometer, respectively. GC-MS was carried out on a Hitachi RMU-6E mass spectrometer combined with a Hitachi gas chromatograph, Model K-53, using a 10% PEG-20M column. Optical rotations were measured in $CHCl_3$ with a Perkin-Elmer Model 141 polarimeter and CD spectra in CCl_4 with a JASCO ORD/UV-6 machine. Column chromatography was carried out with Mallinckrodt silicic acid (100 mesh). Thin layer chromatography (TLC) was performed on Merck Kieselgel GF_{254} with chloroform or chloroform-methanol (97:3 and 95:5) as the developing solvent.

Isolation of Sargatriol (3)——*Sargassum tortile* (dried, 500 g), collected at Wakasa Bay, Fukui Prefecture, in January 1973, was extracted with ether (3 l) at room temperature. The ether extract was concentrated to 0.5 l and the residue was washed with dil. Na_2CO_3 to remove acidic substances. The ether layer was then washed with 3% HCl and dil. Na_2CO_3 successively, dried ($MgSO_4$), and concentrated under reduced pressure. The residue (*ca.* 35 g) was chromatographed on silica gel (350 g, 4.6×45 cm) and eluted with hexane, hexane-ether (7:3, 5:5, and 3:7), ether, CH_2Cl_2, and CH_2Cl_2-MeOH (9:1 and 7:3) successively. Fractions eluted with hexane-ether (2:8 and 3:7) were combined (11 g) and rechromatographed on silica gel. The eluate (6.6 g) with hexane-ether (1:1) was subjected to preparative TLC to give sargatriol (**3**) as a pale yellow oil (550 mg). $[\alpha]_D^{21}$ $+16.0°$ ($c=1.0$, $CHCl_3$). UV λ_{max} nm (ϵ): 232 (24700), 266 (5300), 275 (4580), 335 (2560). IR ν_{max} cm^{-1}: 3400, 1590, 1100, 860. NMR δ: 1.33 (3H, s, *tert*-CH_3), 1.58, 1.65 (each 6H, vinyl $CH_3\times4$), 2.10 (3H, s, toluene CH_3), 3.80 (1H, d, $J=8$ Hz, $>C\underline{H}OH$), 4.30 (1H, dd, $J=8$ and 8.5 Hz, $>C\underline{H}OH$), 4.9—5.6 (3H, olefinic H), 5.53, 6.25 (each 1H, pair of d, $J=10$ Hz, olefinic H), 6.32, 6.48 (each 1H, pair of d, $J=2.5$ Hz, aromatic H). MS m/z: 426 (M^+), 408, 392, 273, 175 (base peak), 137, 69.

Methylatin of Sargatriol (3) with Diazomethane——Sargatriol (145 mg) was treated with excess diazomethane (freshly generated from nitrosomethylurea) in ether overnight and the solvent was removed by evaporation. The oily residue (150 mg) was separated by preparative TLC to give the corresponding methyl ether (**4**) (22 mg) and a carbamate (**5**) (65 mg) together with the unreacted starting material (45 mg).

The methyl ether (**4**): $[\alpha]_D^{23}$ $+16.2°$ ($c=1.42$, $CHCl_3$). IR ν_{max} cm^{-1}: 3560, 1590, 1465, 1220, 1050, 840. NMR δ: 1.35 (3H, s, *tert*-CH_3), 1.58—1.65 (12H, vinyl CH_3), 2.15 (3H, s, toluene CH_3), 3.72 (3H, s,

OCH_3), 3.77 (1H, d, $J=7$ Hz, $>$C$\underline{\text{H}}$OH), 4.28 (1H, dd, $J=7$ and 8 Hz, $>$C$\underline{\text{H}}$OH), 4.83—5.77 (3H, olefinic H), 5.53, 6.27 (each 1H, d, $J=10$ Hz, olefinic H), 6.37, 6.54 (each 1H, d, $J=3$ Hz, aromatic H). MS m/z: 440 (M^+), 422, 407, 287, 189 (base peak), 175, 151, 81, 69.

The carbamate (**5**): IR ν_{max} cm^{-1}: 3500, 1730, 1460, 1230, 1150, 1100, 865. NMR δ: 1.36 (3H, s, *tert*-CH_3), 1.58—1.62 (12H, vinyl CH_3), 2.13 (3H, s, toluene CH_3), 2.85 (3H, d, $J=5$ Hz, NH-C$\underline{\text{H}}_3$), 3.77 (1H, d, $J=7.5$ Hz, $>$C$\underline{\text{H}}$OH), 4.28 (1H, dd, $J=7.5$ and 8.5 Hz, $>$C$\underline{\text{H}}$OH), 4.9—5.56 (3H, olefinic H), 5.51, 6.27 (each 1H, pair of d, $J=10$ Hz, olefinic H), 6.57, 6.71 (each 1H, d, $J=3$ Hz, aromatic H). MS m/z: 426 (M^+-CH_3NCO), 408, 392, 175, 57 (base peak, CH_3-HN^+=C=O).

Acetylation of Sargatriol (3)———Sargatriol (3: 150 mg) was treated with acetic anhydride (1.5 ml) and pyridine (1.5 ml) and the reaction mixture was allowed to stand overnight at room temperaure. The mixture was poured into ice-water and extracted with ether. The ether extract was washed successively with 3% HCl and dil. Na_2CO_3, dried ($MgSO_4$), and concentrated to leave an oily residue. The residue (145 mg) was subjected to preparative TLC to afford sargatriol triacetate (**6**: colorless oil 130 mg). $[\alpha]_D^{19}$ $+34.1°$ ($c=1.0$, $CHCl_3$). IR ν_{max} cm^{-1}: 1735, 1235, 1120, 960, 860. UV λ_{max} nm (ϵ): 228 (34780), 267 (5520), 277 (4420), 320 (3310). NMR δ: 1.35 (3H, s, *tert*-CH_3), 1.58 (6H, vinyl CH_3), 1.66 (3H, br s, vinyl CH_3), 1.72 (3H, br s, vinyl CH_3), 1.99, 2.03 (each 3H, s, alcoholic OAc), 2.24 (3H, s, phenolic OAc), 2.14 (3H, s, toluene CH_3), 5.05 (2H, olefinic H),18) 5.18 (1H, d, $J=8$ Hz, $>$C$\underline{\text{H}}$OAc), 5.50 (1H, t, $J=7$ Hz, olefinic H), 5.52 (1H, d, $J=10$ Hz, olefinic H), 5.72 (1H, dd, $J=9.5$ and 8 Hz, $>$C$\underline{\text{H}}$OAc), 6.26 (1H, d, $J=10$ Hz, olefinic H), 6.54, 6.67 (each 1H, d, $J=2.5$ Hz, aromatic H). MS m/z: 552 (M^+, $C_{33}H_{44}O_7$, Calcd: 552.3087; Found: 552. 3092), 537, 510, 492, 450, 432, 315, 273, 217 (base peak), 175, 69.

Lithium Aluminum Hydride Reduction of Sargatriol Triacetate (6)———A stirred solution of sargatriol triacetate (**6**: 18 mg) in ether was treated with 10 mg of $LiAlH_4$ and the mixture was stirred for 3 h at room temperature. The reaction mixture was treated as usual to give an oily residue (16 mg). Purification of the residue by preparative TLC afforded 10 mg of a colorless oil, whose spectral data (IR and NMR) and *Rf* value on TLC ($CHCl_3$: MeOH 95 : 5) were identical with those of sargatriol.

Periodic Acid Oxidation of Sargatriol (3)——An aqueous solution of 0.05 M HIO_4 (0.2 ml) was added to a solution of sargatriol (12 mg) in dioxane (1 ml), and the mixture was stirred for 1 h at 0°C. Then a small amount of water (2—3 ml) was added, and the whole was extracted with ether. The extract was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. The oily residue was subjected to preparative TLC to afford two products.

The less polar product (**7**) (3 mg): IR ν_{max} cm^{-1}: 2750, 1665. NMR δ: 1.62, 1.70 (each 3H, br s, vinyl CH_3), 2.17 (3H, d, $J=1.5$ Hz, vinyl CH_3), 5.10 (1H, m, olefinic H), 5.90 (1H, br d, $J=8$ Hz, olefinic H), 10.10 (1H, d, $J=8$ Hz, CHO). MS m/z: 152 (M^+), 137, 123, 109, 94, 84, 69, 41 (base peak). This compound was shown to be identical with geranial (**7**) by direct GC-MS comparison with an authentic sample.

The more polar product (**8**) (4.5 mg): IR ν_{max} cm^{-1}: 2730, 1670. NMR δ: 1.32 (3H, s, *tert*-CH_3), 1.65 (3H, br s, vinyl CH_3), 2.12 (3H, s, toluene CH_3), 5.95 (1H, m, olefinic H), 6.12, 6.50 (each 1H, d, $J=10$ Hz, olefinic H), 6.29, 6.44 (each 1H, d, $J=2.5$ Hz, aromatic H), 9.42 (1H, s, CHO). MS m/z: 272 (M^+), 229, 214, 175 (base peak), 137, 91, 81.

Catalytic Hydrogenation of Sargatriol Triacetate (6)———Sargatriol triacetate (**6**: 52 mg) was dissolved in methanol (10 ml) and the solution was hydrogenated in the presence of 10% Pd-C (5 mg) at atmospheric pressure for 3 h at room temperature. The mixture was filtered and the filtrate was concentrated under reduced pressure. The oily residue (40 mg) was purified by preparative TLC to give the phenol acetate (**9**). $[\alpha]_D^{21}$ $+0.6°$ ($c=1.44$, $CHCl_3$). IR ν_{max} cm^{-1}: 1745, 1470, 1200, 1020, 900. NMR δ: 0.86 (12H, *sec*-$CH_3\times4$), 1.25 (3H, s, *tert*-CH_3), 1.76 (2H, t, $J=7$ Hz), 2.14 (3H, s, toluene CH_3), 2.23 (3H, s, phenolic OAc), 2.27 (2H, t, $J=7$ Hz, benzylic H), 6.60, 6.66 (each 1H, d, $J=3$ Hz, aromatic H). MS m/z: 444 (M^+, $C_{29}H_{48}O_3$, Calcd: 444.3603; Found: 444.3554), 402, 319, 137 (base peak), 69.

Hydrolysis of the Phenol Acetate (9)———A solution of the above phenol acetate (**9**) (18 mg) in 2 ml of methanol containing one drop of conc. HCl was refluxed for 1 h. After cooling, methanol was removed by evaporation under reduced pressure. The residue was made alkaline with dil. Na_2CO_3 and extracted with CH_2Cl_2. The CH_2Cl_2 extract was dried ($MgSO_4$) and concentrated. The residue (14 mg) was purified by preparative TLC to give the corresponding phenol (**10**) (colorless oil, 12 mg). $[\alpha]_D^{20}$ $+1.6°$ ($c=1.32$, $CHCl_3$). IR ν_{max} cm^{-1}: 3570, 1610, 1465, 1140. UV λ_{max} nm (ϵ): 299 (3300). NMR δ: (12H, *sec*-$CH_3\times4$), 1.32 (3H, s, *tert*-CH_3), 1.73 (2H, t, $J=6.5$ Hz), 2.11 (3H, s, toluene CH_3), 2.68 (2H, t, $J=6.5$ Hz, benzylic H), 6.37, 6.47 (each 1H, d, $J=3$ Hz, aromatic H). This compound was shown to be identical with the hexahydro compound of δ-tocotrienol (**1**) by IR and NMR comparisons.

Sargatriol Acetonide (11)———A solution of sargatriol (**3**) (20 mg) and *p*-toluenesulfonic acid (1 mg) in 2,2-dimethoxypropane (5 ml) was refluxed for 0.5 h. After cooling, the mixture was made alkaline with dil. $NaHCO_3$ and extracted with ether. The ether solution was dried (K_2CO_3) and concentrated and the residue (23 mg) was subjected to preparative TLC to give the oily acetonide (**11**) (17 mg). $[\alpha]_D^{27}$ $+16.6°$ ($c=1.56$, $CHCl_3$). IR ν_{max} cm^{-1}: 3350, 1590, 1230, 1035, 890, 860. NMR δ: 1.33 (3H, s, *tert*-CH_3), 1.43 (6H, s, *gem*-CH_3), 1.59 (6H, br s, vinyl CH_3), 1.64 (6H, br s, vinyl CH_3), 2.11 (3H, s, toluene CH_3), 3.97 (1H, d, $J=8.5$ Hz, $>$C$\underline{\text{H}}$O–), 4.47 (1H, t, $J=8.5$ Hz, $>$C$\underline{\text{H}}$O–), 5.06 (1H, m, olefinic H), 5.17 (1H, d, $J=9$ Hz, olefinic H), 5.50 (1H, t,

J=7.5 Hz, olefinic H), 5.53, 6.25 (each 1H, d, J=10 Hz, olefinic H), 6.30, 6.46 (each 1H, d, J=2 Hz, aromatic H). MS m/z: 466 (M^+), 451, 408, 391, 314, 256, 175 (base peak), 136, 69.

Hydrolysis of the Acetonide (11)——A solution of the acetonide (**11**) (20 mg) and *p*-toluenesulfonic acid (1 mg) in methanol (0.5 ml) was allowed to stand for 4 h at room temperature. Methanol was removed by evaporation and the residue was purified by preparative TLC to give an oil (8 mg), whose IR and NMR spectra and optical rotation were identical with those of sargatriol (**3**).

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