The yield of α-naphthaldehyde was determined by VPC (internal reference, eicosene) using two columns: SE 30, 2% on HMDS WAW, 1.5 m; Carbowax HMDS (treated with 3% H_3PO_4), 15% on HMDS WAW 60/80, 2 m. Benzaldehyde was detected by VPC using two columns: SE 30, 1% on WAW 60/80, 1 m; the previous Carbowax column.

When α-diketones were formed, the irradiation mixture was treated overnight with acetic anhydride–pyridine. After the usual workup, the products were purified by TLC and recrystallized. β-Diketones and keto enol acetates were identified by comparison with authentic samples.

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Registry No. 1, 73354-52-6; 2, 73354-53-7; 3, 73354-54-8; 4, 60857-46-7; 5, 40327-51-3; 6, 19804-64-9; 7, 19804-81-0; 8, 66-77-3; 9a, 78498-88-1; 9b, 78498-89-2; 10, 66-99-9; 11a, 78498-90-5; 11b, 78498-91-6; 12a, 78498-92-7; 12b, 78498-93-8; 13, 51583-97-2; 14, 57114-80-4; 15, 6327-79-3.

Decaryiol, a New Cembrane Diterpene from the Marine Soft Coral *Sarcophyton decaryi*

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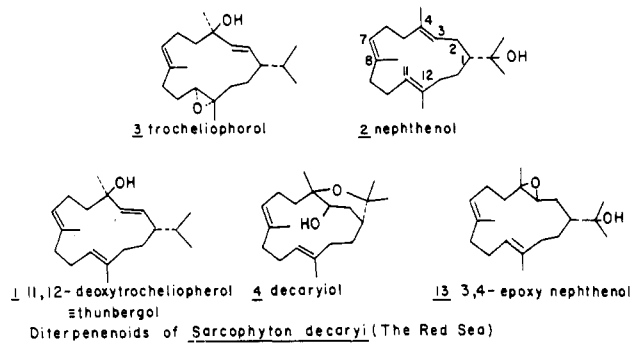
The petroleum ether extract of the soft coral *Sarcophyton decaryi* yielded the cembrane-type diterpenes thunbergol (1), decaryiol (4), and 3,4-epoxynephthenol (13) in addition to nephthenol and trocheliophorol as reported previously. Compounds 4 and 13 are new and were characterized by spectral data, degradative studies by ozonolysis, and chemical transformations. Nephthenol reacts with tetrabromocyclohexadienone to give 11, the 3-bromo analogue of decaryiol. Compounds 4 and 11 rearrange to an enol ether (10), thereby proving the cembranoid structure of 4. 3,4-Epoxynephthenol (13), the second new cembranoid, is believed to be the biogenetic precursor of decaryiol (4), and, indeed, 13 could be transformed into 4 by acid catalysis.

Sarcophyton decaryi (Tixier-Durivault, 1946) is one of many soft corals which populate the coral reefs of the Gulf of Eilat. More than 150 species of these alcyonaceans which form large patches on the reef table have already been reported.[1] Many of the soft corals contain cembranoid diterpenes, some of which are toxic to fish and are believed to play a role in the protection of the soft corals from predators. Other cembranoids have been reported to have biological activities.[2]

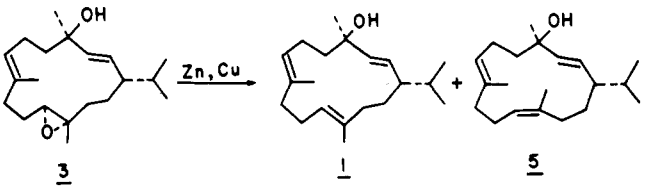
Repeated chromatography of the petroleum ether extract of *S. decaryi* (Sephadex LH-20 and silica gel; see Experimental Secion) yielded, apart from large amounts of glycerides and steroids, five cembranoid diterpenes which were, in order of their polarity, thunbergol (1), nephthenol (2), trocheliophorol (3), 3,4-epoxynephthenol (13), and 4, which was named decaryiol (Chart I). Structure elucidation of two of these compounds, nephthenol (2) and the then unknown trocheliophorol (3), was described by us in a recent report.[3]

Thunbergol, one of the reported 2,7,11-cembratrien-4-ol isomers, was first obtained from the North American Douglas fir *Pseudotsuga menziesii*.[6] The close relationship between thunbergol and trocheliophorol (3) can be seen in the ^1H and ^{13}C NMR spectra (see Table I and the Experimental Section). Furthermore, microozonolysis[4] of 1 gave levulinaldehyde and, in addition, 2-methyl-2-hydroxypentane-1,5-dial, also obtained from 3. Deoxygenation of 3 with Zn/Cu couple[5] gave two olefinic isomers

Chart I



Scheme I



(see Scheme I) in the ratio 9:1 as determined by ^{13}C NMR. The (11*E*)-11,12-deoxytrocheliophorol isomer was identical in all respects with thunbergol. Presumably 3 arises from thunbergol by regiospecific epoxidation, well-known among the marine soft coral metabolites.[7]

Comparison of the ^{13}C NMR spectra of compounds 1, 3, and 5 made possible the almost full line assignment (see Table I). Assignments were based on the peak multiplicities (SFORD), chemical shift considerations,[8] and com-

(1) Y. Benayahu and Y. Loya, *Helgol. Wiss. Meeresenters.* **30**, 362 (1977).
(2) (a) B. Tursch, et al., *Tetrahedron*, **31**, 129 (1975); (b) A. J. Weinheimer, and J. A. Matson, *Tetrahedron Lett.*, 1295 (1977); (c) I. Ne'eman, L. Fishelson, and Y. Kashman, *Toxicon*, **12**, 593 (1974).
(3) A. Groweiss, Y. Kashman, D. J. Vanderah, B. Tursch, P. Cornet, J. Braekman, and D. Daloze, *Bull. Soc. Chim. Belg.*, **87**, 277 (1978).
(4) B. P. Moore and W. V. Brown, *J. Chromatogr.*, **60**, 157 (1971).
(5) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
(6) (a) B. Kimland and T. Norin, *Acta Chem. Scand.*, **22**, 943 (1968); ref 11, p 299. (b) T. Kato, M. Suzuki, M. Takahashi, and Y. Kitahara, *Chem. Lett.*, 465 (1977). (c) The stereochemistry of thunbergol establishes also the C-4 configuration of trocheliophorol (3).
(7) (a) Y. Kashman and A. Groweiss, *J. Org. Chem.*, **45**, 3814 (1980); (b) B. Tursch, J. C. Braekman, D. Daloze, and M. Kaisin in "Marine Natural Products", P. Scheuer, Ed., Academic Press, New York, 1978, p 247.
(8) F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden, London, 1978.

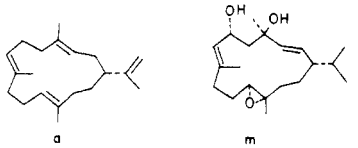
0022-3263/81/1946-4279$01.25/0

Table I. ^{13}C NMR Spectral Data of 2,7,11-Cembratrien-4-ols

C	multiplicity[a]	compd 1	3	5	m[9]
1	d	46.0	46.9	49.0	46.8
2	d	129.2	130.0[b]	130.5	130.4
3	d	138.2	138.3	138.8	137.1
4	s	72.6	72.6	73.0	71.4
5	t	43.0	43.2	42.1	52.4
6	t	22.6	22.5	23.4	64.4
7	d	125.2	129.8[b]	125.2[b]	133.0
8	s	132.4[b]	131.6	132.4[c]	135.4
9	t	36.9	36.4[d]	36.9	35.7[d]
10	t	23.8	25.1	26.1	24.9
11	d	125.2	61.7	124.8[b]	61.0
12	s	128.5[b]	60.0	135.7[c]	59.3
13	t	39.2	35.2[d]	40.7	36.7[d]
14	t	27.7	28.2	29.9	28.0
15	d	33.0	32.7	32.2	33.1
16	q	20.5	20.5	20.5	20.4
17	q	19.5	19.6	19.5	19.0
18	q	28.1	28.2	26.9	28.8
19	q	15.2[c]	15.9[c]	15.2	16.1
20	q	14.7[c]	16.4[c]	17.0	16.1

[a] Assignments of multiplets were made by off-resonance spin decoupling. [b-d] These assignments may be interchanged (see footnote e). [e] Some of the considerations taken into account while assigning the δ values follow. On the basis of the model compound (m), carbons C-18 and C-1 to C-4 (the *E* disubstituted allylmethylcarbinol moiety) and carbons C-15 to C-17 (the *i*-Pr group) could be immediately determined. The two remaining methyl quartets (δ 15.2 and 14.7 in the case of compound 1) were assigned to C-19 and C-20, respectively, on the basis of the 2.3-ppm shift of the latter in compound 5 (in comparison to 1), due to removal of the γ effect between C-10 and C-20. Also easy to identify were C-7 and C-8 (the double bond C atoms) and C-11 and C-12 (the epoxide atoms) of compound 3. In compounds 1 and 5, however, each possessing two double bonds, the Δδ values for each pair of corresponding signals seem to be too small for unequivocal line assignment. The six remaining methylene signals could be divided clearly into two groups, (C-5,9,13 and C-6,10,14). The first one belonging to C-5, C-9, and C-13 appears between 36 and 44 ppm. Among the three atoms, C-5, being strongly influenced by the vicinal C-4 methyl and OH groups, resonates most downfield. The differentiation between C-9 and C-13, however, has not been achieved, as the effects of the Δ^{11} epoxidation[10] and Δ^{11} isomerization on the δ values of the neighboring α- and β-carbon atoms are not equivocal. Distinction between the C atoms of the second group was achieved by comparison with the model compound m. The 22–23-ppm signal, having no countersignal in m, was assigned to C-6 (being a carbinol in m).

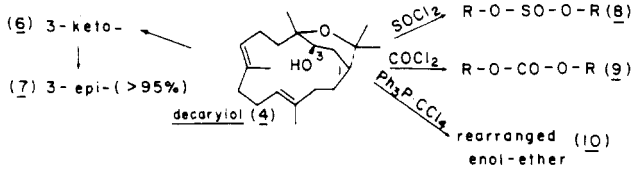
parisons with suitable model compounds. Comparison of the shifts of C-11 and C-12 of **3** and their neighbors with the corresponding shifts in 11,12-epoxy-2,7-cembradiene-4,6-diol[9] (m) suggested the α configuration for the 11,12-epoxide in **3**.



a m

The fourth diterpene, **4**, [mp 126–128 °C; $[\alpha]^{24}_D$ + 69° (c 1.3, $CHCl_3$)] was shown to have the molecular formula $C_{20}H_{34}O_2$ (*m/e* 306). The infrared bands at 3610 and 3480 cm^{-1} together with loss of water in the mass spectrum suggested that this compound was also an alcohol. The ^1H NMR spectrum indicated the presence of two *E* trisubstituted double bonds [6 H (s) at δ 1.57, 1 H (br d) at δ 5.26, and 1 H (br d) at δ 4.89], one CHOR moiety (1 H, dd, δ 4.20), and three methyls adjacent to oxygen (three 3 H, δ 1.10, 1.12, and 1.16). The methyl signals, the deduction that only one hydroxyl group was present (no hydroxyls remained after oxidation of **4** to **6**, vide infra), and the ^{13}C NMR data (three oxygen-bearing C atoms, Table II) pointed to an ether (see unit c, Chart II). Extensive decoupling studies and chemical shift values suggested the partial structural units a–c (see Chart II for these units and for assignment of almost all the protons). As decaryiol (**4**) contains only two double bonds (^{13}C NMR, Table II), moieties a and c could be linked to each other through unit b (in a manner indicative of the unit numbers). Units a–c account for 17 of the 20 carbon atoms in the molecule, the remaining ones being three $OCCH_3$ groups.

Scheme II. Reaction of Decaryiol[a]



[a] decaryiol ≡ RH.

The four unsaturations in **4** (three of which are two double bonds and an ethereal bridge) suggested that the fourth was a carbocycle. According to the above data and the following arguments, decaryiol was proposed to be 4,15-oxido-3-hydroxy-7,11-cembradiene. This structure (unequivocally established by obtaining compound **10** either from compound **4** or from nephthenol (**2**), see Scheme III) was first suggested on the basis of the following experimental results.

(a) Microozonolysis of decaryiol gave levulinaldehyde,[4] confirming the existence of a 1,5-diene moiety in **4**. Decaryiol must, therefore, possess a C-7,C-8 double bond so that the ethereal bridge ($C(Me)-O-C(Me)_2$) has to be either from C-15 to C-4 or from C-15 to C-12 (in order to fulfill the requirement of three methyls next to an oxygen atom).

(b) Jones oxidation of **4** to give a saturated ketone **6** (ν_{max} 1710 cm^{-1}) indicated the presence of a secondary alcohol function and excluded any allylic positions as candidates for the hydroxylation site. The fact that **6** exhibited only one two-proton signal, for protons α to a carbonyl group, reduced still further the possible positions of the OH group. The same conclusion could be reached by considering that the CHOH signal of **4** was coupled to only two vicinal protons. This left either C-3 or C-5 as the OH site if the ether was attached to C-4, or C-11 or C-13 if the the oxygen bridge bearing carbon was C-12. The difference between C-4 and C-12 results from the Δ^7 double bond position.[11] If one presumes, however, the presence of the regular $\Delta^{3,7,11}$-cembratriene double bond sequence, an assumption supported by the two CCH_2CH_2C units observed in the ^1H NMR spectrum as well as the formation of levulinaldehyde, the only possible structure is the 4,15-oxido-3-hydroxy isomer (see Chart II).

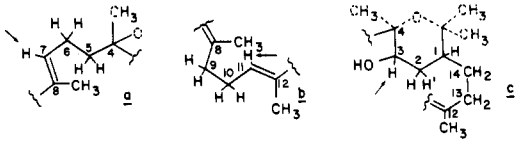
(9) D. Behr, I. Wahilberg, T. Nishida, C. Enzell, J. Berg, and A. Pilotti, *Acta Chem. Scand., Ser. B*, **B34**, 195 (1980).
(10) W. G. Anderson, Chang Y. Byon, M. Gut, and F. H. Bissett, *Tetrahedron Lett.*, 2193 (1976).
(11) A. J. Weinheimer, C. W. J. Chang, and J. A. Matson, *Prog. Chem. Org. Nat. Prod.*, **36**, 287 (1979).
(12) A. J. Weinheimer, J. A. Matson, M. B. Hossain, and D. van der Helm, *Tetrahedron Lett.*, 2923 (1977).

Table II. ^{13}C NMR Spectral Data of Various Substituted 7,11-Cembradienes

C	multiplicity[a]	compd a[19]	2	4	6	8[h]	11	13
1	d	46.0	48.5	40.0	41.3	40.2	43.8	44.1
2	t	32.4	28.6[b]	29.0	35.3	28.0, 27.1	31.6	29.7
3	d	121.8	126.2[c]	70.4	215.5 (s)	74.5, 73.0	55.4	63.0
4	s	133.8	134.1[d]	77.0	81.3	75.4	76.3	61.9
5	t	38.9	39.5[e]	38.2	38.3	37.6, 37.4	37.8	39.9
6	t	24.9	24.6[f]	23.8	23.2	23.7	23.9	23.6
7	d	124.0	125.9[c]	127.9[b]	125.3[b]	127.5	127.0[b]	125.9
8	s	134.8	133.2[d]	133.0[c]	135.9[c]	133.4	133.3[c]	133.8
9	t	39.4	37.9[e]	36.5[d]	37.4[d]	36.2[b]	36.3[d]	36.6
10	t	23.7	24.0[f]	25.3	26.1	25.3	25.0	24.9
11	d	125.9	125.0	128.6[b]	127.3[b]	128.5, 128.3	128.1[b]	123.9
12	s	133.4	133.0	132.6[c]	131.8[c]	132.8, 132.6	133.0[c]	134.9
13	t	34.0	39.0[e]	39.4[d]	39.2[d]	39.2[b]	39.3[d]	39.1
14	t	28.2	28.4[b]	25.3	28.8	25.3	25.0	28.1
15	s	149.2	73.8	75.2	74.6	75.4	75.7	73.3
16[g]	q	110.1 (t)	27.7[f]	22.3	21.6	22.2	22.1	26.6
17[g]	q	19.3	29.8[f]	29.7	29.8	29.6	29.7	28.6
18	q	18.0	15.6	24.3	25.4	25.3	27.6	16.9
19	q	15.5	15.6	15.2	14.9	15.3	15.2	16.0
20	q	15.3	15.6	14.8	14.4	14.8	14.8	15.5

[a] See footnote *a* in Table I. Compound *a* = cembrene-A. [b-f] These assignments may be interchanged (see footnote *i*). [g] Carbon 16 is the equatorial Me in compounds **4**, **6**, **8**, and **11**, and C-17 is the axial one. [h] All the duplicated signals in the spectrum of **8** are of equal intensity. [i] Self-evident are the lines of C-1 and C-3 (the only two sp^3 carbon atoms). Although the chemical shift difference in **4** between C-4 and C-15 (the two tertiary oxygen-bearing atoms) is minimal (less than 2 ppm), an assignment could be suggested on the basis of 4.5-ppm shift of the line assigned to C-4 in compound **6** as compared to that in **4**, as expected from a methylene α to carbonyl.[20] The chemical shift differences between the two trisubstituted double bond signals in the various compounds are minimal, avoiding (except for compounds **4** and **8**) unambiguous assignments. As with the former group of compounds (Table I), the methylene signals could be divided into several groups which were assigned, in order of increasing field strength, to C-5,9,13 to C-2 and C-14, and to the most high-field group, C-6 and C-10. The lines in the 37–38-ppm region are assigned to C-5 on the basis of the duplicity of the corresponding line in **8**. Also straightforward is the C-2 and C-14 determination, based on the larger fluctuation of C-2 in the various compounds caused by derivation of C-3. The differentiation between C-9 and C-13 and between C-6 and C-10, however, does not seem to be unequivocal and needs further clarification. Finally, methyls **19** and **20** were determined to be the most upfield quartet, as in compounds **2** and **a** and in the trocheliophorol group. Among the remaining three, the 24.3-ppm quartet in **4** is assigned to C-18, being most affected by the OH/Br replacement.

Chart II.[a,b] Structure Units a–c of Decaryiol 4



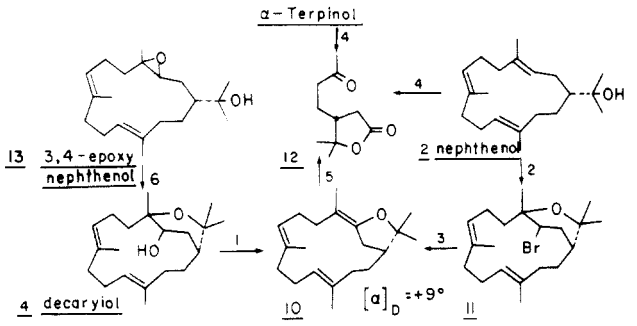
H	δ	J, Hz	H	δ	J, Hz	H	δ	J, Hz
7	5.26 brdd	3.8, 10.0	11	4.89 brdd	11.4, 4.0	3	4.20 dd	12.3, 5.7
6	2.62 dddd	15.7, 10.0, 10.5, 3.8	10	2.49 ddt	15.7, 11.4, 3.8	2	1.72 ddd	12.3, 5.7, 2.0
6′	2.25 dddd	15.7, 10.0, 3.8, 3.0	10′	2.20 m		2′	1.28 dt	12.3, 11.5
5	1.80 ddd	14.4, 10.5, 3.0	9,9′	1.95 m		1	1.60 ddt	11.5, 3.0, 2.0
5′	1.50 ddd	14.4, 10.0, 3.8				14	0.89 ddt	12.3, 11.5, 3.8
						14′	1.30 ddt	12.3, 8.0, 3.0
						13,13′	2.03 dd	8.0, 3.8

[a] The arrows indicate the starting points of the interpretation. [b] The dashed atoms are suggested on arguments other than the ^1H NMR ones (see text).

(c) The coupling constants of 12.3 and 5.7 Hz of the double doublet of the CHOH group indicate that it represents an axial proton in a six-membered ring in agreement with the suggested structure. Furthermore, reduction of the carbonyl of **6** gave only one alcohol (**7**) which differs from **4** (see Scheme II) and whose CHOH signal, a triplet, suggests that it represents an equatorial six-membered-ring proton. Formation of a single epimer upon reduction of **6** is best explained by the highly (penta) substituted tetrahydropyrane (THP) ring which permits only axial approach of the reducing reagent. Strong 1,3-diaxial interactions seem to be responsible for a somewhat twisted chair conformation of the THP ring (see Scheme IV), a conformation which can explain the various coupling constants.

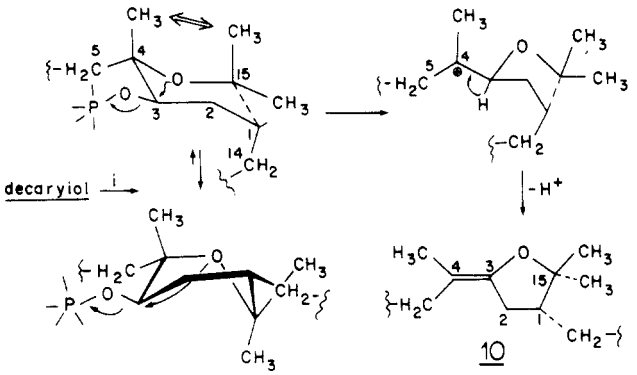
Further support for the 3-hydroxy THP structure was expected to be obtained from an elimination product. Treating decaryiol (**4**) with $SOCl_2$–pyridine gave, instead of the desired olefin, the corresponding sulfite (**8**) as outlined in Scheme II. Interesting in the ^1H and ^{13}C NMR spectra of **8** was the duplication of the signals of H-3, C-3, and several other neighboring C atoms which resulted from the presence of the chiral S atom of the sulfite as there is no element of symmetry which can interchange the above atoms in the two decaryiol units of **8**. Treatment of decaryiol with phosgene gave a similar 2:1 product (**9**, Scheme II; however, no duplication in the NMR was observed, as expected from a planar carbonate. Acidic elimination conditions (boiling of **4** in benzene in the presence of oxalic acid) also failed to give the desired olefin.

Scheme III[a]



[a] (1) $Ph_3P{\cdot}CCl_4$; (2)  (TBCO); (3) $AgClO_4$; (4) O_3, H_2O_2; (5) O_3, Ph_3P; (6) *p*-TsOH.

Scheme IV. Rearrangement of Decaryiol (4) to the Enol Ether 10



[a] i, $Ph_3P{\cdot}CCl_4$. The stereochemistry at C-4 in compound 4 and 10 is unproved.

The explanation for the above behavior can be found in the particular substitution pattern of the THP ring. The ring is prevented from flipping into a conformation in which the leaving group (OR) can occupy the axial position required for E_2 elimination.

Treatment of 4 with $Ph_3P{\cdot}CCl_4$, which usually substitutes OH for Cl and can in special cases cause an E_2 elimination,[7a,13] resulted in loss of a molecule of water; however, a simple dehydration process was not involved as the ^1H NMR spectrum showed no vinyl proton signal. The structure of the product 10 (Scheme III) was suggested on the basis of the ^{13}C NMR spectrum [C=C—O: δ 105.4 (s), 142.6 (s)]; for the reasons discussed above, no simple E_2 elimination was possible. In the absence of a proton with the correct geometry for elimination, the neighboring ethereal oxygen, suitably located for an internal substitution process, migrates to give, after removal of a proton, the enol ether 10 (see Scheme IV).[14] The formation of the energy-rich P→O bond together with the 1,3-diaxial strain release are the driving forces for this rearrangement.

As the biosynthesis of 4 (vide infra) can be visualized as starting from 3,4-epoxynephthenol,[12] we thought it interesting to try and simulate the THP ring closure. For this purpose we reacted nephthenol (2) with tetrabromocyclohexadienone (TBCO), a reagent known to produce Br^+ ions.[15] Formation of the bromonium ion can then be followed by internal nucleophilic attack of groups like OH, with the proton of the OH group subsequently being abstracted by the tribromocyclohexadienone anion.[15] The main product after 18 h was a monobromide ether (11, Scheme III, $C_{20}H_{33}BrO$) with a ^1H NMR spectrum which resembled the spectrum of decaryiol (4; see Experimental Section). The appearance of a proton next to a bromine [δ 4.81 (dd, J =12.3, 5.2 Hz) as compared to the CHOH signal of 4 at δ 4.20 (dd, J = 12.3, 5.7 Hz)] showed clearly that the C-15 OH has attacked a tertiary position which can be either C-4 or C-12. Solvolysis of the bromide with $AgClO_4$ in aqueous acetone, in an attempt to obtain decaryiol (or its epimer 7), yielded instead enol ether 10 with the same rotation, $[\alpha]^{24}_D$ +9°, as the substance obtained from 4. Since the absolute configuration of nephthenol at C-1 is known (1*R*),[16] the absolute configuration of C-1 in 4 followed.

Unequivocal independent proof for the structure of compound 10 was obtained from ozonolysis of nephthenol (2),[17] compound 10, and α-terpinol,[18] all of which produced homoterpenyl methyl ketone (see Scheme III). The mechanism of the formation of 10 from each of the starting materials determines the relative configuration at C-3 and C-4. However, the absolute configuration at these atoms is not established, as the C-3,C-4 double bond in the biogenetic precursor can be attacked from both sides due to the high mobility of the 14-membered macrocycle.

The fifth compound, which was isolated from the crude extract in minute quantities as an oil, was 13 ($C_{20}H_{34}O_2$). The ^1H NMR spectrum of 13 displayed the following signals: δ 2.82 (dd, 1 H) and 1.31 (s, 3 H) [$\overline{OCH-C(CH_3)}$], 5.12 (m, 2 H) and 1.60 (br s, 6 H) [two CH=C(Me) groups], 1.17 (s) and 1.22 (s) (two methyl carbinols). These absorptions as well as other spectral data (including the ^{13}C NMR spectrum; see the Experimental Section and Table II), suggested that 13 was an epoxynephthenol. When 13 was left for several days in $CDCl_3$, it was transformed to compound 4 as evidenced by the ^1H NMR spectrum. The same reaction occurred on addition of traces of *p*-TsOH to a solution of 13 in $CHCl_3$ (see Scheme III). The latter reaction established the structure of 13 as 3,4-expoxynephthenol.

Internal nucleophilic attack of the C-15 OH grouping of 13 on the epoxide to give decaryiol (4) is believed by us to also be the biogenesis of 4.

Table II summarizes the ^{13}C NMR data of decaryiol (4), three of its derivatives (6, 8 and 11), epoxynephthenol (13), nephthenol (2), and cembrene-A[19] (a), with the latter two serving as model compounds. The signal assignment follows the same rationale as with the compounds described in Table I.

As mentioned above, the chiral sulfur atom of the sulfite (8) causes duplication of several of the proton and carbon signals, a phenomenon which assisted in the assignments. A ^1H NMR double-irradiation experiment revealed H-11 to be the duplicated signal in 8 (H-7 remaining as a single broad doublet). One can thus assume that C-11 and C-12, rather than C-7 and C-8, should also be doubled. On the

(13) R. Appel and H. D. Wihler, *Ber.*, **109**, 3446 (1976).

(14) Suitable ^{13}C NMR models of proper enol ethers [E. Taskinen, *J. Org. Chem.*, **43**, 2773, 2776 (1978)] revealed only a small difference between methyl groups cis and trans to the oxygen (Δδ = 1–2 ppm). Since we had on hand only one isomer and found quite large δ value differences for the sp^2 carbon atoms between 10 and the model compounds, the C-3,C-4 geometry determination seems to be equivocal.

(15) T. Kato, et al., *Chem. Lett.*, 518, 1187, 1191 (1976); 565 (1977).

(16) B. Tursch, J. C. Braekman, and D. Daloze, *Bull. Soc. Chim. Belg.*, 84, 767 (1975).

(17) Originally, nephthenol was oxidized by Lemieux oxidation.[16]

(18) O. Wallach, *Justus Liebigs Ann. Chem.*, **275**, 151 (1893); **277**, 110 (1893).

(19) D. F. Wiemer, J. Meinwald, G. D. Prestwich, and I. Miura, *J. Org. Chem.*, 44, 3950 (1979).

(20) A Δδ value of 5.1 ppm is measured for the C-2 atoms in cyclohexanol and cyclohexanone.

basis of this assumption a tentative assignment is also suggested for 4.

Experimental Section

IR spectra were recorded on a Perkin-Elmer Model 177 spectrophotometer. Mass spectra were recorded on a Du Pont 21-491B spectrometer. Optical rotations were measured on a Bellingham and Stanley polarimeter using a 10-cm microcell. ^1H NMR spectra were recorded on JEOL JMN-C-60-HL, Bruker WH-90, or Bruker WH-270 NMR spectrometers, and ^{13}C NMR were recorded on a Bruker WH-90 (22.63 MHz) NMR spectrometer; all chemical shifts are reported with respect to Me_4Si (δ 0). Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are reported uncorrected.

Collection and Extraction of the Soft Coral. The soft coral *Sarcophyton decaryi* (Tixier-Durivault, 1946) was collected by hand at a depth of 3–10 m in the Gulf of Eilat in July 1977. The soft coral was deep frozen immediately after collection and then freeze-dried to give the dry material (1 kg). Dry soft coral (100 g) was extracted with petroleum ether in a Soxhlet apparatus for 24 h. Evaporation of the extract gave a green gum (7 g, 7% dry weight).

Isolation of Cembranes 1–4 and 13. The crude extract (7 g) was applied to a column of silica gel (100 g), and material was eluted with solvent of gradually increasing polarity from petroleum ether through ethyl acetate. Fraction 2, eluted with 8% ethyl-acetate in petroleum ether, contained a mixture of compounds 1 and 2. Fraction 2 was rechromatographed on silica gel with 5% ethyl acetate in petroleum ether as eluant to yield alcohol 1 (65 mg, 0.065% dry weight) and nephthenol (2; 150 mg, 0.15% dry weight). Fraction 3, eluted with 16% ethyl acetate in petroleum ether, contained a mixture of trocheliophorol (3), decaryiol (4), and 3,4-epoxynephthenol (13). Fraction 3 was rechromatographed on Sephadex LH-20 with chloroform/petroleum ether (65:35) as the eluant to yield trocheliophorol (3; 1.3 g, 1.3% dry weight) and a mixture of 3, 4, and 13 from which compound 4 was crystallized out. Recrystallization from acetone–petroleum ether gave 4 (170 mg, 0.17% dry weight). Rechromatography of the mother liquid on LH-20 gave 13 (60 mg, 0.06% dry weight).

(2*E*,7*E*,11*E*)-4-Hydroxy-2,7,11-cembratriene,[6b] deoxytrocheliophorol (1): an oil; $[\alpha]^{24}_D$ +87° (*c* 2.2, $CHCl_3$); IR ($CHCl_3$) 3700, 3620, 3450, 2950, 1450, 1390, 1240, 1210 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.82 (3 H, d, J = 6.5 Hz), 0.85 (3 H, d, J = 6.5 Hz), 1.34 (3 H, s), 1.52 (3 H, br s), 1.61 (3 H, br s), 5.04 (2 H, m), 5.23 (1 H, dd, J = 15.6, 8.3 Hz), 5.7 (1 H, d, J = 15.6 Hz); mass spectrum (EI, 70 eV), *m/e* (relative intensity) 290 (M^+, $C_{20}H_{34}O$, 2), 272 (4), 257 (2), 228 (10), 120 (17), 80 (53), 68 (100).

(1*R*,7*E*,11*E*)-4,15-Oxido-3-hydroxy-7,11-cembradiene, decaryiol (4): crystals (acetone–petroleum ether); $[\alpha]^{24}_D$ +69° (*c* 1.3, $CHCl_3$); mp 126–128.5 °C; IR (CCl_4) 3610, 3480, 2970, 1470, 1430, 1380, 1365, 1145, 1120, 1060, 1020 cm^{-1}; ^1H NMR (see discussion); mass spectrum (EI, 17 eV), *m/e* (relative intensity) 306 (M^+, $C_{20}H_{34}O_2$, 53), 288 ($M^+ - H_2O$, 100), 273 (13), 263 (33), 248 (15), 245 (13), 219 (13), 205 (20). Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.39; H, 11.10.

(1*R*,7*E*,11*E*)-3,4-Epoxy-15-hydroxy-7,11-cembradiene, 3,4-epoxynephthenol (13): an oil; $[\alpha]^{24}_D$ +7° (*c* 1.3, $CHCl_3$); IR ($CHCl_3$) 3400, 2970, 1650, 1240, 1030 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.17 (3 H, s), 1.22 (3 H, s), 1.31 (3 H, s), 1.60 (6 H, br s), 2.82 (1 H, dd, J = 9.2, 4.4 Hz), 5.10 (2 H, m); mass spectrum (EI, 12 eV), *m/e* (relative intensity) 306 (M^+, $C_{20}H_{34}O_2$, 36), 288 (73), 273 (20), 270 (30), 245 (40), 206 (38), 135 (100).

The physical data of compounds 2 and 3 were found to be identical to those described in the literature.[3]

Zn–Cu Couple Reduction of 3.[5] A mixture of 3 (250 mg) and freshly prepared Zn–Cu couple (10 g) in absolute methanol (10 mL) was heated under reflux for 16 h. The precipitate was filtered off and washed with petroleum ether, and the solution was evaporated under reduced pressure to give an oil (160 mg). The oil was chromatographed on a silica gel column (5% ethyl acetate in petroleum ether) to yield, among other products, a 9:1 mixture of 1 and 5 (90 mg, 37% theoretical). The IR, mass, and ^1H NMR spectra of the main isomer were identical with those of 1.

Jones Oxidation of Decaryiol (4). Jones reagent (5 drops) was added to a solution of 4 (30 mg) in acetone (5 mL), and the reaction mixture was stirred at 0 °C for 10 min. Excess reagent was destroyed by addition of methanol. The reaction mixture was then worked up as usual to yield ketone 6: 26 mg (90%); an oil; IR (CCl_4) 2920, 1710, 1450, 1430, 1380, 1365, 1130 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.96 (1 H, ddt, J = 13.1, 10.9, 3.8 Hz), 1.17 (3 H, s), 1.26 (3 H, s), 1.28 (3 H, s), 1.53 (3 H, br s), 1.56 (3 H, br s), 2.59 (2 H, ABX system), 4.78 (1 H, dq, J = 7.6, 1.6 Hz), 4.95 (1 H, br d, J = 10.0 Hz); mass spectrum (EI, 20 eV), *m/e* (relative intensity) 304 (M^+, $C_{20}H_{32}O_2$, 100), 261 (16), 175 (19), 161 (21), 148 (28), 125 (55), 107 (55), 95 (64), 81 (93).

Reduction of Ketone 6 with Sodium Borohydride. Sodium borohydride (50 mg) was added in portions to a solution of ketone 6 (57 mg) in methanol (20 mL), and the solution was stirred at room temperature for 18 h. The solvent was then evaporated and the residue partitioned between water (10 mL) and dichloromethane (3 × 10 mL). The combined dichloromethane phase was dried over anhydrous $MgSO_4$ and the solvent evaporated to give alcohol 7: 36 mg (60% theoretical); IR (CCl_4) 3600, 3480, 2970, 1465, 1430, 1120, 1060, 1025 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.08 (3 H, s), 1.19 (3 H, s), 1.21 (3 H, s), 1.57 (6 H, br s), 4.01 (1 H, t, J = 8.5 Hz), 4.89 (1 H, br t, J = 7.0 Hz), 5.56 (1 H, br t, J = 9.1 Hz); ^{13}C NMR (22.63 MHz, $CDCl_3$) δ 134.0 (s), 133.3 (s), 129.4 (d), 126.5 (d), 78.5 (s), 75.7 (s), 72.8 (d), 39.4 (t), 37.1 (t), 36.4 (t), 36.4 (t), 33.0 (t), 29.9 (q), 29.3 (t), 28.8 (t), 25.8 (t), 25.5 (q), 20.2 (q), 15.1 (2 q); mass spectrum (EI, 70 eV), *m/e* (relative intensity) 306 (M^+, $C_{20}H_{34}O_2$, 5), 288 (50), 273 (1), 263 (10), 248 (2), 81 (100).

Treatment of Compound 4 with Thionyl Chloride. A cold solution of a few drops of thionyl chloride in pyridine (1 mL) was added to a cold solution (0 °C) of 4 (55 mg) in pyridine (1 mL), and the reaction mixture was kept at 0 °C for 1 hr. The pyridine was then evaporated in vacuo and the residue chromatographed on a silica gel H column with 5% ethyl acetate in petroleum ether as eluant to yield compound 8: 46 mg (78% theoretical); IR (CCl_4) 2940, 1370, 1205, 1195, 1140, 1025 (SO), 975, 935, 925 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.92 (2 H, m), 1.13 (6 H, s), 1.16 (6 H, s), 1.21 (6 H, s), 1.59 (12 H, br s), 4.96 (1 H br d, J = 14.1 Hz), 5.00 (1 H, br d, J = 12.5 Hz), 5.13 (1 H, dd, J = 10.0, 6.0 Hz), 5.24 (1 H, dd, J = 10.8, 5.4 Hz), 5.47 (2 H, br d, J = 9.5 Hz); mass spectrum (EI, 12 eV), *m/e* (relative intensity) 305 ($C_{20}H_{33}O_2^+$, 3) 287 (34), 272 (36), 150 (17), 136 (27), 122 (20), 108 (22), 83 (100), 81 (63), 69 (42).

Treatment of 4 with Phosgene. A solution of 10% phosgene in toluene (1 mL) was added to a solution of 4 (38 mg) in pyridine (1 mL), and the solution was kept at room temperature overnight. The solvent was then evaporated in vacuo and the residue chromatographed on silica gel H with 5% ethyl acetate in petroleum ether to yield compound 9: 15 mg (35% theoretical); IR ($CHCl_3$) 2940, 1725, 1380, 1265, 1205, 970 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (1 H, m), 1.14 (3 H, s), 1.16 (3 H, s), 1.59 (6 H, br s), 5.16 (1 H, br d, J = 10.0 Hz), 5.40 (1 H, dd, J = 11.0, 5.2 Hz), 5.40 (1 H, br d, J = 8.0 Hz); mass spectrum (EI, 14 eV), *m/e* (relative intensity) 288 ($C_{20}H_{32}O^{+\cdot}$, 44), 272 (29), 269 (21), 229 (21), 177 (13), 148 (39), 120 (16), 96 (14), 84 (72), 82 (100).

Treatment of 4 with Triphenylphosphine in Carbon Tetrachloride. Triphenylphosphine (100 mg) was added to a solution of 4 (70 mg) in carbon tetrachloride (30 mL), and the reaction mixture was boiled under reflux for 40 hrs. The reaction mixture was then chromatographed on silica gel H using carbon tetrachloride as eluant to obtain 10 (25 mg, 40% theoretical), $[\alpha]^{24}_D$ +9° (*c* 1.45, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.97 (3 H, s), 1.22 (3 H, s), 1.46 (3 H, s), 1.55 (3 H, br s), 1.73 (3 H, br s), 5.00 (1 H, br dd, J = 9.5, 2.5 Hz), 5.14 (1 H, br dd, J = 10.0, 5.9 Hz); ^{13}C NMR (22.63 MHz, $CDCl_3$) δ 142.6 (s), 134.9 (s), 132.1 (s), 128.2 (d), 125.9 (d), 105.4 (s), 75.7 (s), 39.9 (d and t), 36.3 (t), 30.9 (t), 29.0 (t and q), 27.9 (t), 25.2 (t and q), 24.6 (t), 19.0 (q), 16.1 (q), 14.3 (q); mass spectrum (CI, isobutane), *m/e* (relative intensity) 289 (MH^+, 50), 288 (M^+, $C_{20}H_{32}O$, 100), 273 (16), 270 (9), 239 (9).

Bromoetherfication of 2 with 2,4,4,6-Tetrabromocyclohexadienone (TBCO).[15] A mixture of nephthenol 2 (1.5 g) and TBCO (2.4 g) in anhydrous dichloromethane (25 mL) was kept at room temperature for 18 hrs, under N_2 atmosphere. The mixture was then shaken with aqueous 10% sodium hydroxide to remove the resultant tribromophenol (1.5 g). The neutral portion was chromatographed on silica gel H using 2% ethyl acetate in petrol ether as eluant to obtain 11: 800 mg (35%

theoretical); $[\alpha]^{24}_D$ +2° (c 2.65, $CHCl_3$); mp 57-59 °C; IR (KBr) 2940, 1380, 1270, 970 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.89 (1 H, ddt, J = 13.0, 11.2, 3.5 Hz), 1.10 (3 H, s), 1.16 (3 H,s), 1.38 (3 H, s), 1.58 (3 H, br s), 1.59 (3 H, br s), 4.81 (1 H, dd, J = 12.3, 5.2 Hz), 4.87 (1 H, br d, J = 11.0 Hz), 5.27 (1 H, br d, J = 8.0 Hz); mass spectrum (CI, isobutane), m/e 369 (MH^+, $C_{20}H_{33}BrO$, 21), 367 (31), 352 (8), 350 (11), 288 (100), 270 (37).

Treatment of Bromide 11 with Silver Perchlorate. Aqueous solution (0.4 mL) of silver perchlorate (100 mg) was added to a stirred solution of bromide 11 in acetone (0.8 mL). After 1 h at room temperature the solution was filtered to remove salts, and the solvent was evaporated. The residue was chromatographed on silica gel H to obtain the enol ether **10**: 39 mg (65% theoretical); $[\alpha]^{24}_D$ +9° (c 3.0, $CHCl_3$); identical in all respects with the same compound obtained from alcohol **4**.

Ozonolysis of α-Terpinol. Ozone in oxygen was bubbled through a solution of α-terpinol (1.54 g) in ethyl acetate (100 mL) which had been cooled to -78 °C. After 10 min, the excess reagent was removed by warming the solution to room temperature. Following the usual oxidative workup with 30% aqueous H_2O_2 (2 mL), a 1:1 mixture of two epimeric lactols was obtained: 1.73 g (93% theoretical); IR (neat) 3480, 2990, 1710, 1370, 1170 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.85 (3 H, s), 1.00 (3 H, s), 1.10 (3 H, s), 1.25 (3 H, s), 2.05 (6 H, s), 5.40 (2 H, m); ^{13}C NMR (22.63 MHz, $CDCl_3$) δ 208.0, 106.4, 105.3, 84.9, 83.6, 47.5, 45.5, 42.6, 35.9, 35.6, 30.0, 29.2, 27.8, 23.9, 23.4, 22.9. Jones reagent (1 mL) was added to a solution of the above lactols mixture (1.50 g) in acetone (20 mL). After 10 min, a few drops of methanol were added to destroy excess reagent, and the solvent was evaporated. The residue was partitioned between water (10 mL) and dichloromethane (3 × 20 mL). The dichloromethane phase was dried over magnesium sulfate and then evaporated to yield the homoterpenyl methyl ketone **12**: 1.47 g (97% theoretical); IR (CCl_4) 2990, 2970, 1760, 1705, 1420, 1390, 1375, 1270, 1255, 1165, 1125, 1000, 955, 935, 915 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.20 (3 H, s), 1.40 (3 H, s), 2.05 (3 H, s), 2.30 (4 H, m); ^{13}C NMR (22.63 MHz, $CDCl_3$ δ 207.6 (s), 175.4 (s), 86.7 (s), 45.0 (d), 41.7 (t), 34.6 (t), 29.9 (q), 27.3 (q), 23.1 (t), 21.3 (q).

Ozonolysis of Naphthenol (2). Ozonolysis of nephthenol in the same manner as described for α-terpinol gave the same homoterpenyl methyl ketone (**12**).

Microozonolysis[4] of Enol Ether 10. Ozone in oxygen was bubbled through a solution of compound **10** (10 mg) in dichloromethane (10 mL) which had been cooled to -78 °C. After 10 min, the excess reagent was removed by warming the solution to room temperature, and triphenylphosphine (20 mg) was added to the stirred solution. Analysis of the reaction mixture by GC[4] indicated the presence of **12** (identical with **12** which had been obtained from α-terpinol and nephthenol) and levulinaldehyde (identical with an authentic sample).

Treatment of 13 with p-Toluenesulfonic Acid. A solution of **13** (40 mg) and p-toluenesulfonic acid (0.5 mg) in chloroform (2 mL) was kept for 24 h at room temperature. The chloroform solution was then washed with aqueous sodium bicarbonate solution and dried over anhydrous $MgSO_4$. The solvent was evaporated to yield the hydroxy ether **4**: 39 mg (97% theoretical); identical in every respect (NMR, IR, and mass spectra and α_D) with natural decaryiol (**4**).

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Synthesis and Stereochemistry of Thiaspiro-α-methylene-γ-butyrolactones. Single-Crystal X-ray Diffraction Analysis of 2,2,6,6-Tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one

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α-Methylene-γ-butyrolactone systems attached to heterocycles are rare. We reported the synthesis of a few 9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-ones via a Reformatsky-type reaction on substituted 4-thianones. All products were characterized by ^1H and ^{13}C NMR analysis as well as by mass and infrared spectra and elemental analyses. Downfield shifts for C(2,6) in 2,2,6,6-tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one in the ^{13}C NMR spectrum were of such magnitude, compared to model cyclohexyl systems, that the thianone ring was suggested to be flattened near the sulfur end of the molecule. The structure of solid 2,2,6,6-tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one was established by means of an X-ray diffraction analysis of a single crystal and confirmed such a flattening. The molecule crystallizes in the space group $P2_1/c$ with unit cell parameters of a = 6.189 (3) Å, b = 11.244 (4) Å, c = 18.960 (9) Å, and β = 92.39 (4)°. The structure was solved by direct methods and refined by least-squares methods to an R value of 0.057 for 2515 reflections. The five-membered lactone ring is in a flattened twist (C_2) conformation, and the C-O bond has an axial orientation at the 4-position of the thiane ring system.

The diverse biological activities of the compounds having the α-methylene-γ-butyrolactone moiety have been well documented.[1] The possible utilization of these lactones as antitumor agents has attracted the attention of many

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