Treatment of **2b** with excess CH_2N_2 in ether and Kugelrohr distillation gave 295 mg (89% yield based on **1b**) of the methyl ester, bp 40–60 °C (0.4 mm). Gas chromatographic analysis indicated the product is a mixture of esters, arising 99% from **2b** and 1% from **2c**: $[\alpha]^{22}_D$ +38° (*c* 3.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.68 (s, 3 H, CO_2CH_3), 3.50–3.10 (overlapping m, 2 H, H-1 and H-2), 2.18 (s, 3 H, H-8 methyl), 0.88 (d, J = 6 Hz, 3 H, H-9 methyl); IR (neat) 1745, 1725 (C=O) cm^{-1}; mass spectrum, *m/e* (relative intensity) 184 (M^+, 3), 141 (12), 124 (20), 109 (28), 82 (14), 81 (100). The 2,4-DNP derivative of the methyl ester of **2b** was prepared: mp 75–77 °C; $[\alpha]_D$ +160° (*c* 5.1, $CHCl_3$).

Anal. Calcd for $C_{16}H_{20}N_4O_6$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.46; H, 5.50; N, 15.16.

1α,2α,5α-Nepetonic Acid (2c) and Methyl Ester. Treatment of 420 mg (2.62 mmol) of **1c** with ozone and workup in the manner described above gave 360 mg (91% yield) of **2c**; ^1H NMR ($CDCl_3$) lactol forms present, δ 7.50 (br hump, 1 H, acidic H), 3.20–2.80 (overlapping m, 2 H, H-1 and H-2), 2.40–1.00 (5 H, H-3, H-4, and H-5), 2.00 (br humps, 3 H, H-8 methyl), 1.09 (d, J = 7 Hz, 3 H, H-9 methyl).

A portion of this **2c** was treated with CH_2N_2 to give the methyl ester. Gas chromatographic analysis indicated 94% **2c** and 6% **2b**: ^1H NMR ($CDCl_3$) δ 3.65 (s, 3 H, CO_2CH_3), 3.20–2.85 (overlapping m, 2 H, H-1 and H-2), 2.80–1.25 (5 H, H-3, H-4, and H-5), 2.14 (s, 3 H, H-8 methyl), 1.98 (d, J = 7 Hz, 3 H, H-6 methyl); IR (neat) 1745 and 1725 (C=O) cm^{-1}; mass spectrum, *m/e* (relative intensity) 184 (M^+, 4), 129 (45), 127 (23), 109 (26), 100 (35), 81 (89), 43 (100). The 2,4-DNP derivative of **2c** methyl ester melted at 122–123 °C.

Anal. Calcd for $C_{16}H_{20}N_4O_6$: C, 52.73; H, 5.53; N, 15.38. Found: C, 52.63; H, 5.47; N, 15.40.

1α,2β,5α-Nepetonic Acid (2b) from 2c. To 30 mL of aqueous 10% NaOH under N_2 was added 320 mg (1.88 mmol) of **2c**. The solution was magnetically stirred for 2.5 h and then acidified with 10% HCl. The acidified mixture was extracted with ether and the ether extract was dried (Na_2SO_4) and evaporated under vacuum to give **2b** (^1H NMR identical with that described above). Treatment of **2b** with CH_2N_2 and Kugelrohr distillation gave 300 mg (87% yield) of the methyl ester: $[\alpha]^{22}_D$ +35.2° (*c* 3.4, $CHCl_3$); ^1H NMR and IR identical with those described above. The 2,4-DNP derivative of **2b** methyl ester was obtained in 60% yield: mp 78–80 °C; mixed with the 2,4-DNP methyl ester of **2b** obtained from **1b**, mp 76–78 °C; $[\alpha]_D$ +172° (*c* 5.0, $CHCl_3$).

3β,3aβ,6aβ-Nepetolactone (3c) and 3α,3aβ,6α,6aβ-Nepetolactone (3d). A solution of 1.5 g (0.97 mmol) of **1c** in 75 mL of CH_3OH and 1.5 mL of pyridine was ozonized and freed of excess ozone as described for **1b**. The mixture was transferred to an ice bath and 1.5-g portions of $NaBH_4$, each in 15 mL of H_2O, were added to the stirred mixture, one immediately and others after 0.5, 1, 2, and 4 h. The mixture was then acidified with 10% HCl and extracted with ether. The ether extract was washed with $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated to yield 500 mg (36% yield) of a mixture consisting of 65% **3c** and 35% **3d**, as indicated by GC analysis. Lactones **3c** and **3d** were separated by preparative GC. Lactone **3c**: bp 60–65 °C (0.05 mm); $[\alpha]^{24}_D$ +15.1° (*c* 2.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.15 (m, 1 H, H-3), 3.08–1.40 (7 H, CH and CH_2), 1.37 (d, J = 6 Hz, 3 H, H-7), 1.17 (d, J = 7 Hz, 3 H, H-8); mass spectrum, *m/e* (relative intensity) 154 (M^+, 23), 99 (70), 94 (40), 82 (76), 81 (93), 67 (100).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.90; H, 9.26.

Lactone **3d**: bp 60–65 °C (0.05 mm); $[\alpha]^{24}_D$ +78.9° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.69 (m, 1 H, H-3), 3.12–1.40 (7 H, CH and CH_2), 1.37 (d, J = 6 Hz, 3 H, H-7), 1.24 (d, J = 7 Hz, 3 H, H-8); mass spectrum, *m/e* (relative intensity) 154 (M^+, 16), 99 (48), 95 (45), 82 (75), 81 (100), 67 (99).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.25; H, 9.15.

3α,3aα,6α,6aα-Nepetolactone (3a) and 3β,3aα,6α,6aα-Nepetolactone (3b). Lactones **3a** and **3b** were prepared from **1a** by the above procedure in 55% yield. Gas chromatographic analysis indicated the mixture to consist of 42% **3a** and 58% **3b**. Preparative GC gave the pure individual lactones. Lactone **3a**: ^1H NMR ($CDCl_3$) δ 4.31 (m, 1 H, H-3), 2.70–1.30 (7 H, CH and CH_2), 1.36 (d, J = 6 Hz, 3 H, H-7), 1.11 (d, J = 6 Hz, 3 H, H-8); mass spectrum, *m/e* (relative intensity) 154 (M^+, 2), 139 (17), 95 (44), 82 (50), 81 (100), 67 (69). Lactone **3b**: ^1H NMR ($CDCl_3$) δ 4.60 (m, 1 H, H-3), 2.90–1.30 (7 H, CH and CH_2), 1.30 (d, J = 6 Hz, 3 H, H-7), 1.07 (d, J = 6 Hz, 3 H, H-9); mass spectrum, *m/e* (relative intensity) 154 (M^+, 1), 99 (70), 95 (30), 94 (40), 82 (40), 81 (100), 67 (53).

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Registry No. 1a, 21651-62-7; **1b**, 17257-15-7; **1c**, 21651-53-6; **2b**, 21651-52-5; **2b** methyl ester, 6890-02-4; **2b** methyl ester 2,4-DNP derivative, 74366-00-0; **2c**, 58801-35-7; **2c** methyl ester, 74410-38-1; **2c** methyl ester 2,4-DNP derivative, 74410-39-2; **3a**, 74410-40-5; **3b**, 74410-41-6; **3c**, 58845-57-1; **3d**, 58845-58-2.

New Diterpenoids from the Soft Corals *Xenia macrospiculata* and *Xenia obscuronata*

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Sixteen diterpenoids have been isolated from two soft corals of the Red Sea, *Xenia macrospiculata* and *X. obscuronata*. These xenia diterpenoids, many of them novel and reported for the first time, are divided into three subgroups: the xenicins [xeniculin (**2**), 9-deacetoxy-14,15-deepoxyxeniculin (**3**), and 9-deacetoxy-14,15-deepoxyxeniculin 7,8-epoxide (**4**)], the xeniolides [xeniolide-A (**6**), xeniolide-B (**7a**), xeniolide-B 9-acetate (**7b**), 7,8-epoxyxeniolide-B (**8**), and xenialactol (**9a**)], and the xeniaphyllanes [xeniaphyllenol (**11**), 4,5-epoxyxeniaphyllenol (**12**), isoxeniaphyllenol (**13**), 4,5-epoxyisoxeniaphyllenol (**14**), 14,15-xeniaphyllandiol (**15a**), xeniaphyllandiol 14-acetate (**15b**), and 4,5-epoxy-14,15-xeniaphyllandiol (**16**)]. The structures were elucidated from spectral data and chemical transformations. The ^{13}C NMR spectra are fully assigned, and their application to the determination of the xenia diterpenoids is discussed. In addition to the above compounds, another diterpenoid, obscuronatin (**23**), was isolated and its structure elucidated.

The soft corals are known to be a source of many different diterpenoids.[1] Many of these diterpenoids belong to a single chemical class, the cembranoids.[2,3] This report deals with a new group of compounds, the xenia di-

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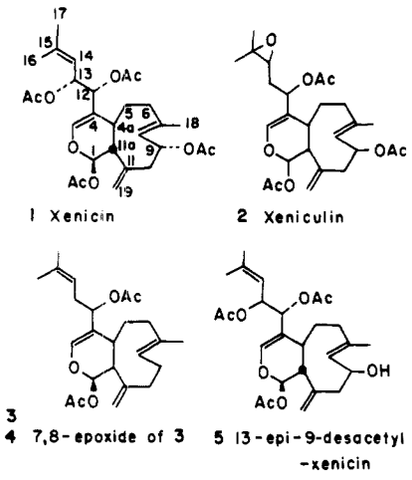
Chart I. Xenicins



terpenoids, believed by us to soon become another prominent class of marine diterpenoids. Included in this group are the xenicins[4,5] and xeniolides[6] as well as the xeniaphyllanes,[5] vide infra, which all appear to be biogenetically closely related to each other. More than 20 members of the group have already been isolated from four different *Xenia* species.

The first representative of the xenicins, xenicin (1, Chart I), isolated from *Xenia elongata*, was disclosed only recently by Schmitz.[4] Characteristic of compound 1 and the entire group is the nine-membered carbocyclic ring, condensed, in the special case of 1, to a dihydropyran ring to give an 2-oxabicyclo[7.4.0]tridecane system. The discovery of 1 was soon followed by the isolation of other closely related compounds[5-7] as well as a second subclass, named xeniaphyllanes, possessing the bicyclo[7.2.0]undecane skeleton as in caryophyllene—all isolated from *Xenia* species. The xeniaphyllanes seem to be either direct intermediates in the biosynthesis of the xenicins or, alternatively, another biosynthetical branch obtained together with the xenicins from a common intermediate. The possible isolation of other related nine-membered-ring natural products may serve to clarify this biogenesis problem.

The isolation of the above-mentioned compounds from *Xenia elongata*,[4] *X. macrospiculata*,[5,6] *X. obscuronata*, and *X. novae-britanniae*[7] seems to indicate that the presence of xenicin-related diterpenoids (including the xeniaphyllanes) is a regular and distinctive chemotaxonomic feature of the genus *Xenia* (there is, of course, a possibility that they could also appear in other marine organisms).

The isolation and structure elucidation of several new compounds of the above group, together with complete data of all the compounds (including those described in two previous short communications)[5,6] are presented in this report.

Table I. Percent Natural Abundance of the *Xenia* Diterpeoids[a]

compd no.	formula	*X. macrospiculata* Aug 1977	*X. macrospiculata* Nov 1977	*X. obscuronata*, July 1978
2	$C_{26}H_{36}O_8$	0.17[b]	0.01[b]	
3	$C_{24}H_{34}O_5$			0.05[b]
4	$C_{24}H_{34}O_6$			<0.01[b]
6	$C_{20}H_{28}O_4$	0.11[c]	0.24[c]	0.13[d]
7a	$C_{20}H_{28}O_4$	0.26[c]	0.21[c]	0.17[d]
7b	$C_{22}H_{30}O_5$	0.01[c]		
8	$C_{20}H_{28}O_5$		0.02[c]	
9a	$C_{20}H_{30}O_4$	0.28[c]	0.07[c]	0.09[d]
11	$C_{20}H_{32}O$	0.10[b]	0.23[b]	0.08[b]
12	$C_{20}H_{32}O_2$	<0.01[b]		
13	$C_{20}H_{32}O$	traces	0.05[b]	
14	$C_{20}H_{32}O_2$		0.01[b]	0.01[b]
15a	$C_{20}H_{34}O_2$		0.07[c]	0.03[d]
15b	$C_{22}H_{36}O_3$		0.07[b]	
16	$C_{22}H_{36}O_4$		0.01[b]	
23	$C_{20}H_{34}O$			0.10[b]

[a] Percentage of the compound in the dry, soft coral. [b] Petroleum ether extract. [c] Ethyl acetate extract. [d] CH_2Cl_2 extract.

The various reported compounds were isolated from two collections of *Xenia macrospiculata* from the Gulf of Eilat and one collection of *Xenia obscuronata* from the Gulf of Suez, the Red Sea. The two collections of the first *Xenia* were made in August and November 1977 and that of the second *Xenia* in July 1978. The petroleum ether and ethyl acetate extracts of the freeze-dried soft corals (or CH_2Cl_2 extracts in the case of *X. obscuronata*; ca. 3–4% dry weight of each animal)[8] were chromatographed on silica gel. Repeated chromatographies of selected fractions on silica gel and Sephadex LH-20 gave eight compounds from the first collection of *Xenia macrospiculata* and 11 compounds from the second collection, six being common to both collections. Nine compounds were isolated from *Xenia obscuronata*, of which three compounds differed from those isolated previously from *X. macrospiculata*. Details of the composition of the three collections, together with molecular formulas, are given in Table I. The discussion regarding the structures of the various isolated diterpenoids (except for one, obscuronatin (**23**)) is divided into two major parts. The first part deals with the 2-oxabicyclo[7.4.0]tridecane compounds, the xenicins, as well as the corresponding lactones, the xeniolides, while the second part describes the xeniaphyllanes possessing the bicyclo[7.2.0]undecane structure. The classification of the various compounds to one of the above structural groups is achieved simply according to the ^1H and ^{13}C NMR data (Tables II–VII). Thus, for example, the xenicins exhibit in the ^1H NMR high-field region only three Me groups, in comparison to four in the xeniaphyllanes, and show in the low-field region two very characteristic sharp doublets belonging to H-1 and H-3. Very helpful in the xeniaphyllanes' structure elucidation, on the other hand, are the ^{13}C chemical shifts of several of the C atoms belonging to the caryophyllene bicyclo[7.2.0]undecane skeleton, vide infra (Table VII).

The first xenicin-related compound, xeniculin (**2**),[9] which we isolated from the petroleum ether extract of *Xenia*

(1) (a) B. Tursch in "Marine Natural Products", Vol. 2, P. J. Scheuer, Ed., Academic Press, New York, San Francisco, and London, 1979; (b) D. J. Faulkner, *Tetrahedron*, **33**, 1421 (1977).
(2) A. J. Weinheimer, C. W. J. Chang, and J. A. Matson, *Fortschr. Chem. Org. Naturst.*, **36**, 285 (1979).
(3) B. N. Ravi and D. J. Faulkner, *J. Org. Chem.*, **43**, 2127 (1978), and references contained therein.
(4) D. J. Vanderah, P. A. Steudler, L. S. Ciereszko, F. J. Schmitz, J. D. Extrand, and D. Van der Helm, *J. Am. Chem. Soc.*, **99**, 5780 (1977).
(5) A. Groweiss and Y. Kashman, *Tetrahedron Lett.*, 2205 (1978).
(6) Y. Kashman and A. Groweiss, *Tetrahedron Lett.*, 4833 (1978).
(7) J. C. Braekman, D. Daloze, B. Tursch, J. P. Declercq, G. Germain, and M. Van-Meerssche, *Bull. Soc. Chim. Belg.*, **88**, 71 (1979).

(8) In comparison to many other soft corals, for example, *Sarcophyton*, *Sinularia*, and *Cladiella* sp., the *Xenia*'s total organic compound content is quite poor.
(9) We named compound **2** xeniculin rather than 13-deacetoxy-14,15-epoxyxenicin since not all of the chiral centers in **2** could be unequivocally assigned.

Table II. ^{1}H NMR Chemical Shifts of the Xenicins[a]

	1[b]	2	3	4	5
H-1	5.86 d	5.86 d	5.87 d	5.95 d	5.88 d
H-3	6.58 d	6.57 d	6.49 d	6.51 d	6.52 d
H-8	5.27 br d	5.27 br d	5.36 br t	2.97 dd	5.26 br d
H-9	5.70 br t	5.67 br t			4.73 br t
H-12	5.38 d	5.54 t	5.28 t	5.27 t	5.34 d
H-13	5.82 t				5.70 dd
H-14	5.08 br d	2.73 t	4.99 br t	4.97 br t	5.15 br d
CH_3-16	1.84[c] s	1.30 s	1.68[c] br s	1.67[c] br s	1.76[c] s
CH_3-17	1.84[c] s	1.30 s	1.66[c] br s	1.62[c] br s	1.76[c] s
CH_3-18	1.74[c] s	1.72 s	1.65[c] br s	1.32 s	1.66[c] s
H-19	4.96 s	4.98 s	4.87 s	5.03 s	4.98 br s
H-19′	4.83 s	4.91 s	4.79 s	4.89 s	4.87 br s
OAc	2.08 s, 2.06 2 s, 2.04 s	2.07 2 s, 2.04 s	2.05 s, 2.03 s	2.08 s, 2.02 s	2.03 2 s, 2.01 s

[a] Spectra were recorded in $CDCl_3$ at 270 MHz with Me_4Si as internal standard. The values are given in δ units. For coupling constants and multiplicities see the Experimental Section. [b] 220 MHz, ref 4. [c] Tentative assignment.

Table III. ^{13}C NMR Chemical Shifts (ppm) of the Xenicins[a]

	1	2	3	5
C-1	91.7 d	91.9 d	91.8 d	91.9 d
C-3	142.6 d	140.8 d	140.7 d	142.1 d
C-4	113.5 s	116.5 s	115.9 s	113.8 s
C-4a	37.1 d	37.2 d	36.7 d	36.8 d
C-5	30.5 t	30.5 t	30.5 t	30.7 t
C-6	39.9 t	40.0 t	40.0 t	39.6 t
C-7	134.3 s	134.4 s	134.3 s	133.1 s
C-8	126.2 d	126.3 d	124.3 d	131.2 d
C-9	70.6 d	70.6 d	25.0 t	67.8[c] d
C-10	42.9 t	43.0 t	35.4[b] t	46.4 t
C-11	146.5 s	146.9 s	151.2 s	147.5 s
C-11a	49.6 d	49.8 d	49.3 d	49.6 d
C-12	76.4 d	72.2 d	74.9 d	75.0 d
C-13	69.8 d	32.7 t	31.3[b] t	70.1[c] d
C-14	119.6 d	60.8 d	119.0 d	119.8 d
C-15	140.7 s	57.8 s	135.8 s	140.2 s
C-16	18.9 q	19.0 q	18.1 q	18.6 q
C-17	25.6 q	24.6 q	25.7 q	25.9 q
C-18	17.5 q	17.7 q	16.7 q	17.8 q
C-19	116.1 t	116.1 t	113.1 t	115.3 t
OAc	169.5 3 s, 168.8 s, 21.0 4 q	170.3 2 s, 169.3 s, 21.3 2 q, 21.0 q	170.2 s 169.6 s 21.3 q 20.9 q	170.2 s, 169.9 s, 169.6 s, 21.2 q, 20.9 q

[a] Assignments of multiplets were made by off-resonance spin decoupling. [b,c] These assignments may be interchanged.

Table IV. ^{1}H NMR Chemical Shifts of the Xeniolides[a]

	6	7a	7b	8[b]	9a	9b	10a[7]	10b[7]
H-1	4.08 dd				4.60 d	5.49 d	4.07 dd	4.14 dd
H-1′	3.61 t						3.61 dd	3.65 dd
H-3		4.88 d	4.90 d	4.92 d	4.66 d	4.66 d		
H-3′		4.43 d	4.42 d	4.42 d	4.29 d	4.37 d		
H-8	5.32 br d	5.40 br d	5.45 m	3.0[c] m	5.28 d	5.35 br d	5.24 d	2.86 d
H-9	4.78 br t	4.69 dt	5.45 m	3.72 ddd	4.85 m	5.68 br t	4.78 m	3.65 m
H-12	6.92 d	6.06 d	6.06 d	6.07 d	5.84 d	5.89 d	6.39 d	6.41 d
H-13	6.53 dd	6.40 dd	6.43 dd	6.35 dd	6.43 dd	6.44 dd	6.85 dd	6.88 dd
H-14	6.26 d	5.97 d	5.97 d	6.00 d	5.82 d	5.88 d	6.06 d	6.07 d
CH_3-16	1.38 s	1.38 s	1.38 s	1.35 s	1.34 s	1.36 s	1.33 s	1.27 s
CH_3-17	1.38 s	1.37 s	1.38 s	1.35 s	1.34 s	1.25 s	1.33 s	1.27 s
CH_3-18	1.70 br s	1.67 br s	1.72 br s	1.25 s	1.74 br s	1.81 br s	1.67 s	1.35 s
H-19	5.09 s	5.07 s	5.16 s	5.23 s	4.93 s	4.92 s	5.09 s	5.27 s
H-19′	4.91 s	5.00 s	5.07 s	5.16 s	4.75 s	4.86 s	4.95 s	5.06 s
OAc			2.07 s			2.10 s, 2.03 s		

[a] See footnote *a* of Table II. [b] Measured on a 90-MHz instrument. [c] Partially obscured by other peaks.

macrospiculata, was found to possess the same bicyclo system as xenicin (1). The ^{1}H NMR spectra of compound 2 (Table II) was most significant for its structure elucidation.

Comparison of the ^{1}H NMR spectrum of compound 2 with that of xenicin (1) proved unequivocally that the bicyclic skeletons together with their functional groups in both compounds are the same, an assumption which was further strongly supported by the fully analyzed ^{13}C NMR spectra as discussed below. The proton NMR spectra indicated clearly the existence of the followng functional groups: (a) an 1-acetoxydihydropyran moiety [δ 5.86 (d,

Table V. ^{13}C NMR Chemical Shifts (ppm) of the Xeniolides[a]

	6	10a[7]	7a	7b	9a	9b
C-1	71.0 t	71.1 t	173.2 s	172.9 s	99.9 d	97.4 d
C-3	171.2 s	169.1 s	71.6 t	71.5 t	69.8 t	69.8 t
C-4	132.7 s	132.9 s	137.2 s	137.3 s	139.5 s	138.2 s
C-4a	42.7 d	51.0[b] d	37.1 d	37.1 d	44.1 d	43.5 d
C-5	38.0 t	37.8 t	37.5 t	37.4 t	35.5 t	35.5 t
C-6	40.1 t	39.9 t	39.8 t	39.8	40.2 t	40.4 t
C-7	132.7 s	132.9 s	134.3 s	136.0 s	132.9 s	134.1 s
C-8	130.8 d		130.4 d	126.3 d	130.5 d	126.1 d
C-9	67.4 d	67.2 d	70.1 d	72.3 d	67.6 d	70.7 d
C-10	44.8 t	45.6 t	43.6 t	39.8 t	46.9 t	43.9 t
C-11	147.4 s	147.9 s	142.3 s	141.4 s	151.2 s	149.1 s
C-11a	49.4 d	50.0[b] d	57.3 d	57.2 d	57.5 d	53.9 d
C-12	151.1 d	147.9 d	127.6 d	127.7 d	122.2 d	123.6 d
C-13	119.8 d	122.6 d	121.3 d	121.3 d	120.9 d	120.6 d
C-14	136.5 d	136.1 d	145.2 d	145.2 d	142.5 d	143.1 d
C-15	71.0 s	70.9 s	70.9 s	71.0 s	71.0 s	70.7 s
C-16	29.8 q	29.5 q	29.8 q	29.8 q	29.9 q	30.1 q
C-17	29.8 q	29.5 q	29.8 q	29.8 q	30.1 q	30.1 q
C-18	17.5 q	17.4 q	19.2 q	19.3 q	17.7 q	19.3 q
C-19	115.6 t	114.9 t	119.7 t	120.8 t	112.4 t	120.8 t

[a] See footnote *a* of Table III. [b] These assignments may be interchanged.

J = 2.6 Hz, H-1) and 6.57 (d, J = 1.8 Hz, H-3)], (b) a terminal methylene [δ 4.91 (s) and 4.98 (s, H-19,19′)], and (c) an allyl acetate [δ 5.27 (br d, J = 7 Hz, H-8) and 5.67 (br t, J = 7 Hz, H-9)]. The NMR spectra of compounds **1** and **2** were compared in $CDCl_3$ as well as C_6D_6 which is known to possess a strong solvent effect, and in both solvents the skeleton proton signals of **1** and **2** were found to be in very good agreement. It was clear that the differences between compounds **1** and **2** stem from changes in the side chain only. Two methyl groups α to oxygen in **2** were found to replace in the ^1H NMR spectrum two vinylic methyls of **1**; this, together with the disappearance of one of compound **1**'s vinyl protons (at δ 5.08) and the appearance of an epoxy signal at δ 2.73 (t, J = 5.9 Hz, H-14), suggested the 14,15-epoxide in compound **2**. Furthermore, the triplet exhibited by H-14 points to the absence of a 13-OAc group in **2**. The 12-OAc group, on the other hand, remained in the molecule, and its relative position to H-14 was established by a double-irradiation experiment whereupon each one of the H-12 and H-14 protons was found to be coupled with the same C-13 protons. The ^{13}C chemical shifts proved to be a delicate probe for the structure and stereochemical assignments of this system and were especially valuable for the comparison of unknown compounds (like **2**) with compounds **1** and **5**, the structures of which were determined unequivocally by X-ray analysis.[4,7] The ^{13}C chemical shifts of the various xenicin carbons are summarized in Table III; the assigning of the carbon signals was based on the peak multiplicities (SFORD), chemical-shift considerations,[10] and comparisons with suitable model compounds. On the basis of the above rationale, the acetal (C-1), the vinyl ether (C-3 and -4), the other vinyl (C-7, -8, -11, -19, -14 and -15), and the methyl vinyl carbons (Me-16, -17, and -18) could be quite easily identified. C-1 resonates at δ 91.7–91.9 in all four compounds (**1**–**3** and **5**). C-4 in compounds **1** and **5** is slightly upfield shifted as compared to C-4 in compounds **2** and **3** due to the additional C-13 acetate (γ effect). In all the xenicins an E configuration could be assigned to the Δ^7 double bond according to the chemical shifts of Me-18, appearing at δ 17–18 (rather than at 22–25 for the Z configuration)[11] and according to the C-9 position (δ 25.0) in case of compound **3**. A γ effect is also responsible for the δ differences between Me-16 and Me-17. Comparison of the xenicin δ values among themselves enabled the assignments of the acetate-bearing carbon atoms. Thus, a comparison of compounds **1** and **2** suggested the δ 70.6 doublet, appearing in both compounds, to belong to C-9 while the δ 72.2 doublet in the spectrum of **2** was attributed to C-12 [differentiation between C-12 and C-13 in compound **1** was achieved by taking into consideration the neighboring-group effects (as, e.g., the strong Me-16/C-13 γ effect)]. Among the methylene signals, the one appearing at 39.6–40.0 ppm was attributed to C-6, being strongly influenced by the vinyl Me-18 (a β effect), and it also appears in the same range in the xeniaphyllanes and xeniolides (Tables V and VII). Comparing the δ values of compounds **1** and **5** suggested the 42.9-ppm resonance line in **1** to belong to C-10, being shifted by 3.5 ppm as expected[12] by the C-9 OAc-OH exchange, while the remaining two methylenes (C-5 and -6) are almost unaffected. In compound **3**, which lacks the oxygen function at C-9, the C-10 signal appears at 35.4 ppm (almost the same location as in the xeniolides and xeniaphyllanes, Tables V and VII). The distinction between C-4a and C-11a was based on comparison with the iridioid terpenes[13] in which values of 33.0–37.1 and 43.6–47.8 ppm resulted for the corresponding C atoms.

On the basis of the ^{13}C NMR data, it now appears that the stereochemistries at C-1, C-4a, C-11a, and C-9 in compound **2** are essentially the same as those in compound **1**.

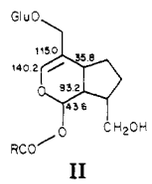
The two other compounds belonging to this group, which were isolated in minute amounts from the petroleum ether extract of *Xenia obscuronata* (compounds **3** and **4**, $C_{24}H_{34}O_5$ and $C_{24}H_{34}O_6$, respectively) were determined to be 9-deacetoxy-14,15-deepoxyxeniculin (**3**) and 9-deacetoxy-14,15-deepoxyxeniculin 7,8-epoxide (**4**). The structures of these two compounds were established mainly by the ^1H and ^{13}C NMR data (Tables II and III) as well as by the mass spectral fragmentations, in the same manner as described above for compound **2**. Characteristic signals for H-1 and H-3 in the ^1H NMR and typical absorptions of C-1,3,4,4a,11a in the ^{13}C NMR determined the dihydropyran moiety. Furthermore, a good correlation between the ^{13}C chemical shifts of the nine-membered ring in 9-deacetoxy compound **3** and in compounds 1, 2, 5, and 17 established the structure of **3** (and **4**). The only determination which was not straightforward was the location of the second acetate (the one in addition to the 1-acetoxy group). Of the six possible locations for a secondary acetate [δ 5.28 (t)] in the molecule, two, C-9 and C-13, could be immediately excluded since the neighboring H-8 and H-14 (appearing as triplets in the ^1H NMR spectrum) each have two vicinal protons. Furthermore, both **3** and **4** show

(10) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York and London, 1972. (b) F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden, Press, New York, 1976.

(11) P. A. Couperus, A. D. H. Clague, and J. P. M. Van-Dongen, *Org. Magn. Reson.*, 8, 426 (1976).

(12) Reference 10a, pp 168, 440.

(13) See structure II for example. S. R. Jensen, R. J. Nielsen, C. B. Mikkelsen, J. J. Hoffmann, S. D. Jolad, and J. R. Cole, *Tetrahedron Lett.*, 3261 (1979).



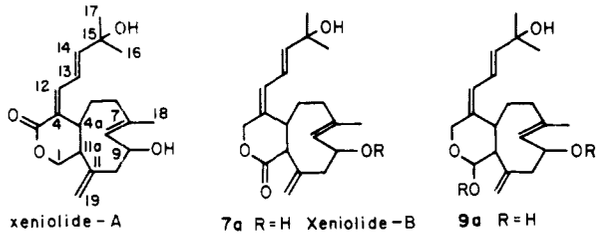
II

Table VI. ^{1}H NMR Chemical Shifts of the Xeniaphyllanes[a]

	17	11	13	15a	15b	19	12	14	16
H-5	5.28 m	5.31 m	5.29 m	5.31 m	5.29 m	2.88 dd	2.90 dd	2.90 dd	2.88 dd
H-19	4.94 s	4.94 s	4.94 s	4.94 s	4.92 s	4.97 s	4.97 s	4.97 s	4.97 s
H-19'	4.82 s	4.83 s	4.83 s	4.83 s	4.83 s	4.85 s	4.85 s	4.87 s	4.86 s
CH_3-20	1.60 br s	1.59 br s	1.60 br s	1.61 br s	1.60 br s	1.20 s	1.18 s	1.19 s	1.18 s
$CH_3$18	0.99 s	1.04 s	0.99 s	0.99 s	0.98 s	1.01 s	1.08 s	1.03 s	1.01 s
H-13		4.46 dt	5.62 br s				4.45 dt	5.60 m	
H-14		5.20 br d	5.62 br s	3.29 dd	4.77 dd		5.20 dt	5.60 m	4.75 dd
CH_3-16		1.70 br s	1.32 s	1.21 s	1.20 s		1.70 br s	1.30 s	1.18 s
CH_3-17		1.70 br s	1.32 s	1.16 s	1.20 s		1.70 br s	1.30 s	1.18 s
OAc					2.12 s				2.12 s

[a] See footnote *a* of Table II.

Chart II. Xeniolides



6 xeniolide-A
10a 4,12Z-isoxeniolide-A
10b 7,8-epoxide of 10a
7a R=H Xeniolide-B
7b R=Ac-B 9-acetate
8 7,8-epoxide of 7a
9a R=H
9b R=Ac

relatively strong $(M - C_5H_9)^+$· fragments in the mass spectra due to the cleavage of the C-12/C-13 bond. Similar multiplicity arguments also excluded C-5. Of the remaining possible carbons, C-12 was preferred over C-6 and C-10, on the basis of ^{13}C chemical shift considerations; C-3 and -4 were found to be shifted by −1.9 (γ effect of C-12 OAc) and +2.4 (β effect) ppm, respectively, compared to compound 1 (the δ values are essentially the same as those in compound 2). C-6 seemed also to be the most unlikely OAc attachment point, as the triplet at 40.0 ppm remained almost unchanged in the whole series. Finally, unequivocal proof for the acetate being at C-12 was obtained by a double-irradiation experiment (as in the case of compound 2); irradiation of each one of the triplets at 5.27 (H-12) and 4.97 ppm (H-14) changed the multiplicity of the H-13 multiplet at 2.30 ppm.

Compound 4, the more polar of the two, is very similar to compound 3, the only difference being the replacement of the 7,8 double bond by an epoxide (this is the first example of such a pair, a total of five being described in this report). As shown below, the 7,8 double bond is also the most sensitive one to chemical oxidation (*m*-chloroperbenzoic acid) as could be shown in the case of caryophyllene and compound 11.

Repeated chromatography of the ethyl acetate extracts of both *Xenia* species gave the xeniolides, an additional group of compounds closely related to the xenicins. The structures of these more polar compounds, xeniolide-A (**6**) and xeniolide-B (**7a**), were previously suggested by us[6] (see Chart II). Additional evidence for the proposed structures resulted from the structures of several new compounds (**7b**, **8**, and **9a**) which are given below. In this context, it was also of special interest to compare xeniolide-A (**6**) with its geometrical isomer, isoxeniolide-A (**10a**) (and its 7,8-epoxy derivative **10b**), obtained by the Belgian group from *Xenia novae-britanniae* together with compound **5**.[7] The difference between isoxeniolide-A, **10a** (and **10b**), and xeniolide-A (**6**) is in the geometry of the 4,12 double bonds, an *E* configuration in the case of **6** (and **7**) as opposed to the *Z* configuration in case of compound **10**.[14] Having on hand both geometrical isomers, the ^{1}H chemical shift values of the suitable protons (H-12 and H-13) could be now used directly for the side-chain structure elucidation of these compounds as well as of the new ones. The nearby carbonyl in compound **6** causes the H-12 signal to be the most downfield appearing one. In compound **10a**, on the other hand, the farthest downfield proton is H-13.[7]

Assignment of the xeniolide ^{13}C signals followed the same methodology as that employed in case of the xenicins, vide supra. A good representative of this group is xeniolide-A (**6**); the various oxygen-bearing C atoms (C-1,9,15) of **6** were determined according to their multiplicities, and the Me-18 was determined by comparison of the ^{13}C NMR spectrum with those of the xenicins (the two other methyls overlap). The δ value of Me-18 established the *E* configuration of the 7,8 double bond. The sp^2 carbons, C-11,19 and C-7,8, could be immediately recognized by comparison of the ^{13}C NMR spectrum with those of the xenicins. Of the remaining signals, the one at 132.7 (s) ppm must belong to C-4 (the only singlet) while the doublet at 151.1 ppm was attributed to C-12 (the β-carbon of an α,β-unsaturated ester).[15] The doublet at 136.5 ppm was attributed to C-14, being strongly influenced by the side-chain terminus (β effects). As a result, C-13 must be assigned at 119.8 ppm. Among the methylenes, the one appearing most downfield [δ 44.8 (t)] was attributed to C-10, which was mostly affected by the C-9 OH/OAc exchange (comparison of **7a** and **7b**), while the 40.1-ppm signal was assigned to C-6 as in the case of the xenicins (Table III) and xeniaphyllanes (Table VII) (the above assignments leave C-5 for the resonance at 38.0(t)). C-4a was distinguished from C-11a by comparison of the spectra of compound **6** with that of its $\Delta^{4(12)}$-*Z* isomer (**10a**)[7] [C-4a is shifted −7.3 (or −8.3) ppm in **6** due to a γ effect of C-13]. The spectra of the other xeniolides were elucidated on the basis of the spectrum of compound **6** by employing arguments such as those given above.

Two additional compounds which accompany xeniolide-A and xeniolide-B in the ethyl acetate extract of the *Xenia* species were determined to be the 9-acetate derivative of xeniolide-B (**7b**) and the corresponding 7,8-oxirane of xenolide-B (**8**), another pair of the 7,8 olefin epoxides. Both compounds (**7b** and **8**) were characterized by their NMR data (Tables IV and V). Furthermore, the structure of compound **7b** was unequivocally confirmed by acetylation of **7a** (Ac_2O/Pyr, room temperature) to give **7b**.

Of special interest was the third compound, xenialactol (**9a**), the most polar one among the ethyl acetate compo-

(14) The possibility of xeniolide-A/isoxeniolide-A isomerization during sun drying has been examined by us. No isomerization could be revealed after either drying the coral in the sun or exposure of the pure compound (or the crude extract) to the sun for 7 days.

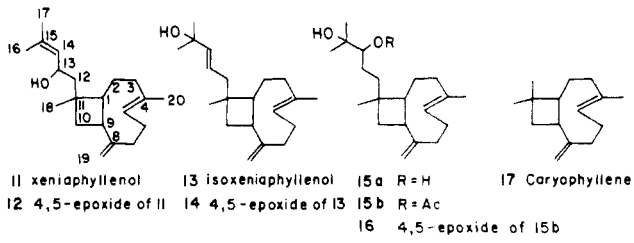
(15) Reference 10a, p 193.

Table VII. ^{13}C NMR Chemical Shifts (ppm) of the Xeniaphyllanes[a]

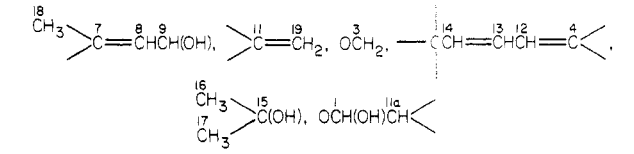
	m[i]	17	11 ($\Delta\delta$)[h]	13	15a	15b	19 ($\Delta\delta$)[h]	12	14	16	18	20 ($\Delta\delta$)[h]	21
C-1	d	53.7	52.3 (1.04)	51.6	52.6	52.8	50.8 (0.91)	49.4	48.7	50.2	51.8	51.9 (0.91)	51.3
C-2	t	28.5[b]	28.7[b] (0.26)	28.7[b]	28.4[b]	28.3[b]	27.2[b] (1.17)	27.4[b]	27.9[b]	28.0[b]	g	28.9 (1.04)	26.5
C-3	t	40.1[c]	39.9 (0.13)	39.8[c]	39.9[c]	39.8[c]	39.1 (3.90)	39.0[c]	39.0[c]	39.0[c]	g	39.9 (0.78)	39.0
C-4	s	135.0	135.1 (0.52)	135.1	135.3	135.2	59.8 (11.70)	59.8	59.9	59.8	135.8	138.2 (1.30)	59.0
C-5	d	124.5	124.5 (0.26)	124.6	124.5	124.5	63.7 (10.66)	63.9	63.9	63.8	124.9	122.8 (1.69)	61.6
C-6	t	29.5[b]	29.4[b] (0.13)	30.0[b]	30.0[b]	30.0[b]	30.2 (3.12)	30.3[b]	30.2[b]	30.2[b]	g	21.9 (2.47)	24.8
C-7	t	34.9	34.4 (0.26)	34.8	34.7	34.8	29.9[b] (0.65)	29.4[b]	30.2[b]	30.0[b]	g	40.7 (4.16)	37.7
C-8	s	154.5	154.4	154.6	154.6	154.6	151.8 (0.91)	151.8	151.9	151.9	156.1	216.4 (5.20)	214.1
C-9	d	48.6	49.3 (0.91)	48.6	48.5	48.3	48.7 (0.91)	49.4	48.7	48.7	40.0	52.6 (2.99)	52.6
C-10	t	40.6[c]	39.9 (1.43)	38.8[c]	39.0[c]	39.1[c]	39.8 (0.39)	39.3[c]	38.1[c]	38.5[c]	40.4	35.7 (2.86)	35.4
C-11	s	32.9	35.1	36.1	35.9	35.7	34.1 (0.52)	36.1		35.9	32.9	33.5 (1.04)	34.4
C-12	t	30.0[f]	51.2 (5.20)	46.3	41.2	40.4[c]	29.9[f] (0.13)	51.1	46.1	40.5	29.8[f]	29.3[f] (0.13)	29.4[f]
C-13			66.0 d (14.17)	123.4 d	23.3 t	23.9 t		65.9 d	123.0 d	23.9 t			
C-14	d		129.5 (1.95)	140.3	79.4	80.5		129.2	140.7	80.4			
C-15	s		133.7 (3.51)	70.8	73.2	72.3		134.3	70.8	72.5			
C-16	q		18.1 (2.34)	30.0	26.0[d]	25.2		18.1	30.0	25.6[d]			
C-17	q		25.7 (1.56)	30.0	26.6[d]	26.6		25.7	30.0	26.8[d]			
C-18	q	22.6[f]	20.4 (1.17)	20.6	20.0	19.9	21.7[f] (0.26)	19.5	19.7	19.1	22.9[e,f]	21.9[f] (0.65)	22.2[f]
C-19	t	111.8	112.1 (0.52)	112.0	112.0	111.8	112.8 (0.65)	113.0	113.1	113.1	110.3		
C-20	q	16.2	16.4 (0.13)	16.2	16.3	16.2	17.0 (3.38)	17.2	16.8	17.1	23.1[e]	15.9 (0.78)	16.2
OAc						171.2 s, 21.1 q				171.3 s, 21.1 q			

[a] See footnote *a* of Table III. [b-e] These assignments may be interchanged. [f] The C-11 *gem*-dimethyls of the caryophyllenes. [g] The methylene resonance lines (35.4, 28.6, 28.4, and 25.5 ppm) were not assigned. [h] $\Delta\delta$ values (in parts per million) upon addition of 0.56, 0.20, and 0.23 equiv of Eu(fod)$_3$ to compounds **11**, **19**, and **20**, respectively. [i] Multiplicity.

Chart III. Xeniaphyllanes



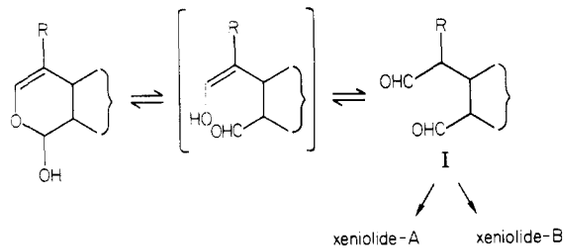
nents. The NMR data suggested the existence in **9a** of the following functional groups (see Table IV for the corresponding chemical shifts and multiplicities and also ref 6):



The groups are reminiscent of the ones present in compounds **6** and **7a**; however, compound **9a** lacks the lactone (IR and ^{13}C NMR). Strong OH absorptions in the IR spectrum (3620, 3450 cm^{-1}), the appearance of 3-hydroxyls [one tertiary hydroxyl, C-15 (δ 71.0 (s)), one secondary OH, C-9 (δ 67.6 (d)), and one lactol, C-1 (δ 99.9 (d)), the two latter moieties undergoing acetylation], and the loss of three molecules of water in the mass spectrometer [*m/e* 316 ($M^+ - H_2O$), 298 ($M^+ - 2H_2O$), and 280 ($M^+ - 3\ H_2O$)] suggested for **9a** a lactol structure closely related to that of compounds **6** and **7**. The acetylation of **9a** gave the diacetate **9b** in which two ^1H signals in the ^1H NMR were paramagnetically shifted as expected [H-1 shifts from δ 4.60 (d) to 5.49 (d) and H-9 from δ 4.8 (m) to 5.68 (br t)]. An AB quartet (rather than an ABX system) appearing at δ 4.29 (d) and 4.66 (d, J = 14 Hz) and resulting from two geminal protons together with the ^1H NMR chemical shifts and the pattern of the side-chain protons (Table IV; confirmed by a double-irradiation experiment) suggested for **9a** the same C-3,C-4 side-chain segment as in xeniolide-B (**7a**) rather than that in xeniolide-A and, hence, suggested that compound **9a** is the corresponding lactol of **7a**. This assumption also agreed with the UV spectrum which resembled the one of **7a** [243 nm (ϵ 15600) in comparison with 241 nm (ϵ 15900) in the case of **7a**]. Final proof for the structure was achieved by mild oxidation of compound **9a** with Ag_2CO_3 on Celite[16] to give **7a** in ca. 25% yield. The particular interest in compound **9a** originates from the biosynthetic point of view. Xenialactol (**9a**) seems to be biogenetically closely related to the xenicins,[17] their biosynthesis starting either from geranylgeraniol pyrophosphate or geranyllinalool pyrophosphate or, alternatively, from the oxidative cleavage product of the four-membered ring of xeniaphyllane. A lactol of type **9a** or 1-deacetylxenicin is expected to be in equilibrium with its open dialdehyde form (I). Dialdehyde I can then, by an oxidation–reduction process (formally a Cannizzaro-type reaction) followed by dehydration, give either xeniolide-A or xeniolide-B. That changes in the side chain are secondary reactions could be seen from the isolation of minute amounts of another xeniolide, which seems to have a saturated 15-hydroxy side-chain (lack of material prevented full structure elucidation).

(16) M. Fetizon and M. Golfier, *C. R. Hebd. Seances Acad. Sci.*, **267**, 900 (1968).

(17) By biogenesis we mean only the synthesis of the skeleton. Further changes such as epoxidation of the 7,8 double bond, hydroxylation at position 9, acetylations, and most likely also changes in the side chain have to be secondary reactions.

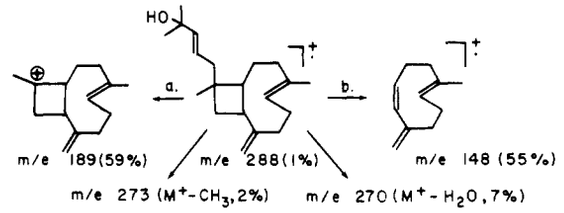


The second major group of compounds that was isolated from both *Xenia* species possesses the bicyclo[7.2.0]undecane caryophyllene skeleton. Table I shows the distribution of seven members of this group (**11–16**, Chart III), which was named the xeniaphyllane group, in the various collections. The structure of the major diterpenoid, xeniaphyllenol (**11**), was previously disclosed by us.[5] The bicyclo[7.2.0]undecane skeleton suggested for this compound was based mainly on the ^{13}C NMR data. Table VII gives the ^{13}C NMR data of compound **11** together with those of the other members of this group (**12–16**) in comparison with the closely related compounds caryophyllene (**17**),[18] isocaryophyllene (**18**),[18] 4,5-caryophyllene oxide (**19**),[19] the 8-keto derivative of **17** (**20**),[20] and the corresponding 8-keto 4,5-oxide (**21**).[20] The latter compounds, **18–21**, were prepared to serve as ^{13}C NMR model compounds. The ^{13}C chemical shifts were found to be an excellent probe for the structure elucidation of these compounds, including their stereochemistries, as could be seen, for example, by comparison of compounds **17** and **18**. Isocaryophyllene (**18**), obtained by a photochemical isomerization of **17**,[18] possessses the *Z* double bond at the 4-position, a change whose influence is not limited to the double bond vicinity only (see Table VII). Thus, C-9 of compound **18** is strongly affected by the Δ^4 isomerization, being shifted by ca. 8.6 ppm diamagnetically due to removal of a strong transannular δ effect. Another strongly influenced carbon is, of course, Me-20, due to removal of the γ effect (also strongly affected are the various methylenes; however, these signals have not been interpreted as yet). The above values indicate clearly the validity of the ^{13}C NMR meausrements for Δ^4-*E*/*Z* assignments in these compounds as well as in the xeniaphyllanes.

Excellent agreement was found on comparison of the ^{13}C NMR spectra of the nine-membered-ring carbons of xeniaphyllenol (**11**) with those of caryophyllene (**17**) (±0.2 ppm). The four-membered-ring carbon signals of compound **11** are shifted slightly, as expected from the side chain substituent effects. The various side chain carbon signals were determined with the aid of an LIS experiment (see Table VII), and those groups neighboring the complexation site could be easily determined. The LIS experiment also helped in the distinction between C-1 and C-9; the former line was found to be more influenced (this line in **11**, in comparison to that in **17**, is diamagnetically affected by the C-13 γ effect).

Differentiation of the various methylenes was not straightforward. Of the five methylenes in **11**, C-3 and C-10 are expected, due to β effects, to resonate farthest downfield (both carbons overlap in the case of compound **11** but separate upon Eu(fod)$_3$ addition). As with the xenicins (Table III, C-10), the triplet at 34.4–34.8 ppm in the Δ^4 compounds is attributed to C-7 (in good agreement with the corresponding values measured in the case of lychnopholic acid,[21] a 2-hydroxycaryophyllenecarboxylic acid, and methylenecyclohexane[10a]), while the remaining triplets at 28.5 and 29.5 ppm are thus attributed to C-2 and C-6. The δ values of C-6 and C-20 confirm the *E* configuration of the C-4,5 double bond, vide supra (distinction between the methyls follwed the same rationale as with the xenicins).

Scheme I. Fragmentation Pattern of Xeniaphyllanes



The spectral assignment of compound **12**, the 4,5-epoxy derivative of **11**, was based on comparisons with the spectra of compounds **11** and **19** (4,5-caryophyllene oxide). In the case of the latter compound, an LIS experiment made possible an unequivocal signal assignment of most of the carbon atoms (see Table VII). From the above as well as from a comparison of compounds **20** and **21** (epoxide and olefin), it is clear that no simple relationships exist between the epoxide and olefin δ values, thus preventing simple δ-value correlations within the pair. The assignments of the other xeniaphyllanes, **13**, **15a**, and **15b**, were based on comparisons with compounds **11** and **17** while the epoxides **14** and **16** were compared with compounds **12** and **19**.

Epoxidation of compound **11** with *m*-chloroperbenzoic acid gave a second epimer in minute amounts. On the basis of ^1H and ^{13}C NMR data, this epimeric epoxide can be easily distinguished from the natural one (**12**; the epoxide proton, H-5, appears at δ 2.99 (dd) as compared to δ 2.90 (dd) in **12**) and thus compounds **12**, **14**, **16**, and **19** must all possess the same stereochemistry.

Further support for the proposed structure of compound **11** was achieved from characteristic mass spectral fragmentations of the bicyclo[7.2.0]undecane system[19] as well as of the side chain (see Scheme I). Xeniaphyllenol (**11**) was found in one collection (Table I) to be accompanied by small amounts of its 4,5-oxirane (**12**), the same type of counterpart as discussed above.

An additional compound, isoxeniaphyllenol (**13**), an isomer of compound **11**, possesses the same bicyclic skeleton (Tables VI and VII) and differs only in the side chain. Having a tertiary hydroxyl group [δ 70.8 (s); does not undergo acetylation] and a disubstituted unconjugated double bond, it is formally an allylic rearrangement product of **11**. The suggested Δ^{13}-15-hydroxy side chain could be confirmed by an LIS experiment. These LIS measurements ($\Delta\delta$, Me-16,17 ≫ H-14 > H-13 > Me-18 > H-19 > H-19′ > Me-20, H-5) clearly determined the location of the hydroxyl to be at C-15. Furthermore, upon addition of sufficient Eu(fod)$_3$, the H-13 and H-14 protons were separated enough to exhibit their mutual coupling constant [for a Eu(fod)$_3$/substrate ratio of 0.9, H-14 appears at δ 9.46 (d, J = 16 Hz) and H-13 at 8.60 (dt, J = 16 and 7 Hz)]. The coupling constant of 16 Hz agrees well with an *E* configuration of the Δ^{13} double bond. Finally, compound **11** was transformed into compound **13** by an allylic rearrangement with the aid of Ph_3P/CCl_4.[22]

(18) K. H. Schulte-Elte and G. Ohloff, *Helv. Chim. Acta*, **51**, 548 (1968).
(19) W. Treibs, *Chem. Ber.*, **80**, 56 (1947). Caryophyllene oxide was prepared by us by monoepoxidation of caryophyllene with *m*-chloroperbenzoic acid.
(20) R. Kaiser and D. Lamparsky, *Helv. Chim. Acta*, **59**, 1803 (1976).
(21) R. E. Raffauf, M. P. Pastore, C. J. Kelly, P. W. Le-Quesne, I. Miura, K. Nakanishi, J. Finer, and J. Clardy, *J. Am. Chem. Soc.*, **100**, 7437 (1978).
(22) R. Appel, *Angew. Chem., Int. Ed. Engl.* **14**, 801 (1975).

Table VIII. NMR Data (in ppm) for 23

$C^8H=C^7(CH_3)$ a		$CH_3C^1(OH)C^2H=C^3HC^4H$ b		$C^{3'}H_2C^{4'}H=C^{5'}(C^{6'}H_3)C^{7'}H_3$ c		$C^{1''}HCH_3$ d	
CH_3-12	1.53 (br s)	CH_3-11	1.18 (s)	CH_3-6′	1.58 (br s)	CH_3-8′	0.83 (d)
H-8	4.49 (br d)	H-2, H-3	5.23 (m, 2 H)	CH_3-7′	1.68 (br s)		
				H-4′	5.05 (br t)		
C-8	126.4 (d)[a]	Me-C_1	31.0 (q)	C-3′	25.5 (t)	C-1′	25.9 (d)
C-7	132.4 (s)	C-1	72.9 (s)	C-4′	125.2 (d)	C-1′ Me	17.2 (q)[b]
C-7 Me	16.8 (q)[b]	C-2	140.1 (d)	C-5′	130.6 (s)		
		C-3	129.1 (d)[a]	C-6′	17.7 (q)		
		C-4	52.1 (d)	C-7′	25.8 (q)		

[a,b] May be interchanged.

Another compound which was isolated from the petroleum ether extract of both *Xenia* species is compound **15b**. As with compounds **11** and **13** (see Tables VI and VII), the NMR data immediately suggested the bicyclo[7.2.0]undecane skeleton, leaving the differences between **15b**, **11**, and **13** to be focussed in the side chain. The IR spectrum (3460, 1735 cm^{-1}), ^1H NMR spectrum [δ 1.20 (s, 6 H), 2.12 (s, OAc), 4.77 (dd, J = 10 and 4 Hz)], and ^{13}C-NMR data [171.2 (s), 21.1 (q), 80.5 (d), 72.3 (s) ppm] indicated a hydroxyl and an acetate group, both located in the side chain. As the compound does not undergo aceylation, the hydroxyl has to be tertiary, and, therefore, a $Me_2C(OH)$ group should be the chain's terminus. The location of the acetate, the α-proton of which possesses only two vicinal protons [δ 4.77 (dd)], should be at either C-12 or C-14. Distinction between the two positions was achieved by hydrolysis of **15b** to the diol **15a** which was subsequently submitted to a $NaIO_4$ microscale oxidation to give the 14-keto **22** [^1H NMR δ 9.95 (t, J = 1.5 Hz)]. Compound **15a** was also found to be a natural product which could have been isolated from the ethyl acetate extract of *Xenia macrospiculata*. (Compound **15a** could be acetylated with Ac_2O/Pyr to give compound **15b**.)

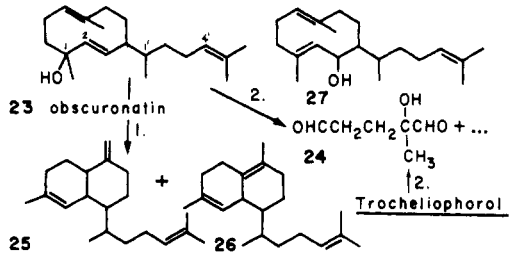
Two additional diterpenoids **14** and **16** were determined to be the epoxy counterparts of **13** and **15b**, respectively. The NMR differences between the olefins and the corresponding epoxides (Tables VI and VII) were the same as those in the cases of compounds **11** and **12** (disappearance of the 5.30-ppm signal due to H-5, with appearance of a doublet of doublets at 2.80–2.90 ppm, as well as shifting of the vinyl methyl from 1.60 to 1.18–1.19 ppm).

Obscuronatin (**23**, $C_{20}H_{34}O$, four unsaturations) is another monocarbocyclic, tertiary alcoholic diterpenoid which was isolated from *Xenia obscuronata*. Compound **23** contains, as shown in Table VIII, three double bonds, and according to its spectral data, it does not belong to the above group of compounds. The ^1H and ^{13}C NMR data for **23** indicated the groups shown in Table VIII.

The alcohol-containing moiety was identified by Eu(fod)$_3$ addition to the ^1H NMR spectrum. This LIS experiment opened up the vinylic proton region, enabling the determination of the H-2, H-3 neighborhood (no protons at C-1 and only one proton at C-4), their Δ^2 trans geometry, and their relation to the complexation site [for an Eu(fod)$_3$/substrate ratio of 0.5, values of δ 5.87 (d, J = 15.6 Hz, H-2) and 6.28 (dd, J = 15.6 and 9.4 Hz, H-3) have been measured].

Next, microozonolysis[23] of **23** was performed to give 2-methyl-2-hydroxypentane-1,5-dial (**24**; a sample of this dialdehyde was obtained from the ozonolysis of trocheliophorol;[24] see Scheme II), thereby confirming the C-2,1,10,9,8 unit and, indirectly, on the basis of the existence of moieties a and b (Table VIII), the whole ten-membered ring except for C-5 and C-6. Support for the rest of the molecule, namely, the eight-carbon side chain, was obtained from the mass spectrum which showed a strong peak at m/e 161 ($C_{12}H_{17}^+$, $M^+ - H_2O - C_8H_{15}$, 46%). A similar fragment was also observed by Bohlmann in the case of 1,7-dimethyl-4-(1′-methylethyl)cyclodeca-2,7-dien-1-ol (isolated from a plant origin).[25] With the assumption of normal biosynthesis and the validity of the isoprene rule, 1,7-dimethyl-4-(1′,5′-dimethyl-$\Delta^{4'}$-hexyl)-cyclodeca-2,7-dien-1-ol was suggested for **23**.

Scheme II. Characterization of Obscuronatin



1. $Ph_3P \cdot CCl_4$ or H^+ 2. O_3

Compound **23** was found to undergo facile water elimination in which a transannular reaction is involved, most probably closing the ten-membered ring of **23** to give the bicyclo compounds **25** and **26**. The suggested structures for compounds **25** and **26** are based on their mass spectra and ^1H NMR data [compound **25** exhibits four vinyl protons in the low-field region at δ 5.53 (br s), 5.12 (br t, J = 7 Hz), and 4.66 and 4.55 (2 s, $=CH_2$) while **26** shows only two at δ 5.41 (br s) and 5.12 (br t, J = 7 Hz)]. (See Scheme II and the Experimental Section.) This transformation takes place slowly under very mild acidic conditions (traces of an acid) or rapidly when Ph_3P/CCl_4 is employed.[22] Both bicyclic compounds (**25** and **26**) gave again in the mass spectra strong m/e 161 peaks (54 and 94%, respectively), indicative of the intact side chain. Comparison of the ^1H NMR spectrum of compound **25** with that of bifluora-4,10(19),15-triene, most recently isolated from a termite soldier,[26] revealed almost complete overlap of the two spectra, suggesting for compound **25** the same structure as that for the termite frontal gland secretion diterpene. Lack of sufficient material prevented us from further study of these two olefines.

It is of interest to note that deliphol (**27**) which is similar to obscuronatin, being an allylic rearrangement product,

(23) B. P. Moore and W. V. Brown, *J. Chromatogr.*, **60**, 157 (1971).
(24) A. Groweiss, Y. Kashman, D. J. Vanderah, B. Tursch, P. Cornet, J. C. Braekman, and D. Daloze, *Bull. Soc. Chim. Belg.*, **87**, 277 (1978).
(25) (a) F. Bohlmann, K. H. Knoll, C. Zdero, P. K. Mahanta, M. Grenz, A. Suwita, D. Ehlers, N. Le-Van, W. R. Abraham, and A. A. Natu, *Phytochemistry*, **16**, 965 (1977); (b) F. Bohlmann and M. Lonitz, *Chem. Ber.*, 111, 254 (1978).
(26) D. F. Wiemer, J. Meinwald, G. D. Prestwich, B. A. Solheim, and J. Clardy *J. Org. Chem.*, **45**, 191 (1980).

was isolated from another marine origin, namely, the brown alga *Dilophus ligulatus*.[27] Finally, it is interesting to note that Bohlmann[25] has isolated the above-mentioned germacrene derivative together with caryophyllene and caryophyllene oxide, pointing to possible similar biosynthetic routes in the plant and the soft coral.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 177 spectrophotometer. Ultraviolet spectra were recorded on Varian Cary 219 and Techtron 635 spectrophotometers in methanol solutions. Optical rotations of $CHCl_3$ solutions were measured with a Bellingham and Stanley polarimeter. Melting-points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Mass spectra were taken with a Du Pont 21-491 B instrument. Parent peaks of the compounds were analyzed on a Varian MAT 731 high-resolution mass spectroscopy instrument.

^{13}C NMR spectra of $CDCl_3$ solutions were measured with a Bruker WH-90 spectrometer (22.63 MHz). ^1H NMR spectra were recorded, unless stated otherwise, on a Bruker WH-270 spectrometer. Chemical shifts are reported in δ values downfield from internal Me_4Si, and the coupling constants are given in hertz. All solvents used were either spectral grade or freshly distilled.

Collection and Extraction of *Xenia macrospiculata*. The soft coral was collected twice at a depth of 3–5 m in Ras-el-Muqebla (the Gulf of Eilat, the Red Sea). The first collection was in August and the second one in November of 1977. In both collections freeze-dried material was ground and extracted in ambient petroleum ether (48 h), in hot petroleum ether in a Soxhlet (24 h), and finally with ethyl acetate or occasionally with dichloromethane for another 48 h. Both petroleum ether extracts were combined, after no differences between them could be revealed. The first collection afforded 470 g of dry material, which gave 9.1 g of petroleum ether crude extract as a viscous brown oil and 8.2 g of ethyl acetate crude extract as a very sticky green gum. In the second collection we had 800 g of dry material which afforded 10.3 g of petroleum ether extract and 12.7 g of ethyl acetate extract.

Isolation of Diterpenoids. First Collection. A 3.5-g sample of the petroleum ether extract was chromatographed on a column of silica gel (40 × 2.5 cm). The material was eluted with solvent mixtures of increasing polarity from petroleum ether to chloroform and then to ethyl acetate. Elution with ethyl acetate–$CHCl_3$ (1:6) gave a fraction (790 mg) which was rechromatographed on a Sephadex LH-20 column (with 7:3 $CHCl_3$–hexane as eluent) and finally again on a silica gel column (elution with $CHCl_3$–hexane, 1:1), to obtain alcohol **11** (200 mg) and its corresponding epoxide **12** (25 mg). The fraction which was eluted with 1:4 ethyl acetate–$CHCl_3$ (1170 mg, including glycerides) was rechromatographed with the aid of high-pressure LC (on a Porasil-A column; elution with ethyl acetate–$CHCl_3$, 1:9) in order to separate xeniculin (**2**) from a mixture of sterols. A more polar fraction, which was eluted with 1:3 ethyl acetate–$CHCl_3$ afforded 340 mg of crystalline **2**, which was recrystallized from benzene–petroleum ether.

A 1.0-g sample of the ethyl acetate extract was chromatographed on a column of LH-20 (40 × 2.5 cm, elution with 2:1:1 hexane–CH_2Cl_2–methanol), and the main fraction (540 mg) was rechromatographed on a short silica-H column (elution with a mixture of CH_2Cl_2 and ethyl acetate with increasing polarity). The fraction eluted with 1:4 ethyl acetate–CH_2Cl_2 gave 30 mg of compound **7b** in ca. 80% purity. Elution with a mixture with a higher percentage of ethyl acetate (40–60%) afforded, in the order of increasing polarity, **6** (50 mg), **7a** (160 mg), and the triol **9a** (50 mg) all as very viscous oils.

Isolation of Diterpenoids. Second Collection. A 6.3-g sample of the petroleum ether crude extract was chromatographed on a silica gel column (25 × 3.5 cm) as described above. The fraction eluted with 1:9 ethyl acetate–$CHCl_3$ (5.0 g, mainly glycerides) was rechromatographed on an LH-20 column (elution with 7:3 $CHCl_3$–hexane) to give alcohol **11** (900 mg) and a mixture of **11** and **13** (260 mg), which was separated with the aid of high-pressure LC (a Porasil-A column, elution with 1:9 ethyl acetate–CH_2Cl_2). This separation afforded more of compound **11** (100 mg) and 70 mg of compound **13**. Alternatively, the latter mixture was acetylated and then chromatographed on a silica gel column in order to separate the acetate of **11** from the tertiary alcohol **13**, which did not undergo acetylation. The fractions that were eluted with 1:3 ethyl acetate–$CHCl_3$ were combined (1.1 g) and rechromatographed on an LH-20 column to give xeniculin **2** (80 mg) and a mixture of three xeniaphyllanes. This mixture was separated by silica gel chromatography to give, in the order of polarity, compounds **15b** (360 mg), **14** (40 mg), and **16** (30 mg), all as oils.

The ethyl acetate extract of this collection was separated by several identical parallel chromatographies; e.g., 660 mg were chromatographed on a LH-20 column (40 × 2.5 cm, elution with 2:1:1 petroleum ether–CH_2Cl_2–methanol), which afforded, in the order of elution, **15a** (45 mg), **6** (100 mg), **7a** (90 mg), **9a** (30 mg), and a minor quantity of **8** (15 mg, in ca. 70% purity). These materials were further purified by chromatography on a prepacked Lobar column (Merck, Kieselgel 60, size A, elution with ethyl acetate under medium pressure).

Collection and Extraction of *Xenia obscuronata*. The soft coral was collected at Ras-Garah (the Gulf of Suez, the Red Sea) in July 1978 and was handled similarly to the above collections. Freeze drying gave 1860 g of dry material, which was extracted with petroleum ether (to give 28.2 g of extract) and then with dichloromethane (to give 21 g of crude extract).

Isolation of Diterpenoids from the Petroleum Ether Extract. A 11.1-g sample of crude extract was chromatographed on a short silica-H column (5 × 5.5 cm). The materials were eluted with solvents of the same polarity gradient as in the chromatography of *X. macrospiculata*. The fractions eluted with mixtures of petroleum ether and 40–60% CH_2Cl_2 (2.5 g, mainly glycerides) were combined and rechromatographed on an LH-20 column (prepared and eluted with 7:3 CH_2Cl_2–petroleum ether) to give 800 mg of obscuronatin (**23**) as an oil and 150 mg of alcohol **11**. The more polar fractions, which were eluted with 7:3 CH_2Cl_2–petroleum ether up to 1:9 ethyl acetate–CH_2Cl_2, were combined and rechromatographed on Sephadex LH-20. This chromatography afforded, in the order of elution, a mixture of 200 mg of compounds **3** and **4**, 250 mg of pure **11**, and a mixture of **11** with **14** (210 mg). The xenicin-like compounds (**3** and **4**) were separated on a short silica-H column. Elution with 1:9 ether–petroleum ether gave pure **3** (100 mg) and **4** (30 mg) as viscous oils.

Isolation of Diterpenoids from the CH_2Cl_2 Extract. The crude extract (8.0 g) was chromatographed in the same manner as the less polar extract, and the main fractions were rechromatographed on a LH-20 column (elution with 2:1:1 hexane–CH_2Cl_2–methanol). The fraction that was eluted with 30% ethyl acetate in CH_2Cl_2 afforded, after the second chromatography, 250 mg of compound **15a**. The 40–50% ethyl acetate fraction gave 900 mg of compound **6**, and the 60–70% ethyl acetate fraction contained 1200 mg of **7a**, while elution with 100% ethyl acetate gave 600 mg of **9a**. A prepacked Lobar column was used for final purification as described above.

Xeniculin (2). See ref 5.

9-Deacetoxy-14,15-deepoxyxeniculin (3): IR (neat) 3075, 2960, 2930, 2860, 1740, 1662, 1450, 1375, 1240, 1150, 1020, 950, 870, 835, 790 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 344(11), 343 (50), 342 (25, M^+ – HOAc), 333 (10), 301 (7), 300 (9), 299 (20), 284 (22), 283 (90), 282 (9, M^+ – 2 HOAc), 269 (16), 81 (23), 57 (100); ^1H NMR 6.49 (d, J = 1.8), 5.87 (d, J = 1.8), 5.36 (br t, J = 7–8), 5.28 (t, J = 7–8), 4.99 (br t, J = 7), 4.87 (s), 4.79 (s), 2.05 (s, 3 H), 2.03 (s, 3 H), 1.68 (br s, 3 H), 1.66 (br s, 3 H), 1.65 (br s, 3 H).

9-Deacetoxy-14,15-deepoxy-7,8-epoxyxeniculin (4): IR (CCl_4) 2960, 2930, 2860, 1735, 1665, 1450, 1375, 1240, 1155, 1115, 1085, 1015, 965, 940, 920, 870 cm^{-1}; mass spectrum (15 eV), *m/e* (relative intensity) 359 (19), 358 (M^+ – HOAc, 100), 349 (30), 316 (19), 307 (32), 299 (6), 298 (8), 265 (15), 247 (23), 229 (25), 201 (7), 175 (8), 173 (9), 162 (23), 157 (25), 129 (72); ^1H NMR 6.51 (d, J = 1.8), 5.95 (d, J = 2.2), 5.27 (t, J = 7–8), 5.03 (s), 4.97 (br t, J = 7), 4.89 (s), 2.97 (dd, J = 10, 3), 2.08 (s, 3 H), 2.02 (s, 3 H), 1.67 (br s, 3 H), 1.65 (br s, 3 H), 1.32 (s, 3 H).

(27) V. Amico, G. Oriente, M. Piattelli, C. Triangali, E. Fattorusso, S. Magno, and L. Mayol, *J. Chem. Soc., Chem. Commun.*, 1024 (1976).

Xeniolide-A (6) and Xeniolide-B (7a). See ref 6.

Xeniolide-B 9-Acetate (7b). This compound was isolated only in ca. 80% purity: IR (CH_2Cl_2) 3500, 2920, 1735, 1640, 1370, 1320, 1240, 1150, 1025, 970, 915, 895, 760 cm^{-1}; ^1H NMR 6.43 (dd, J = 15, 11), 6.06 (d, J = 11), 5.97 (d, J = 15), 5.45 (m, 2 H), 5.16 (s), 5.07 (s), 4.90 (d, J = 13), 4.42 (d, J = 13), 2.07 (s, 3 H), 1.72 (br s, 3 H), 1.38 (s, 6 H).

7,8-Epoxyxeniolide-B (8). This compound was obtained only in ca. 75% purity: ^1H NMR (90 MHz) 6.35 (dd, J = 14, 10), 6.07 (d, J = 10), 6.00 (d, J = 14), 5.23 (s), 5.16 (s), 4.92 (d, J = 11), 4.42 (d, J = 11), 3.72 (ddd, J = 7), 1.35 (s, 6 H), 1.25 (s, 3 H). The epoxide proton (H-8) is part of a complicated signal at δ 3.00.

Xenialactol (9a): $[\alpha]^{25}_D$ −90° (*c* 1.9, $CHCl_3$); UV 243 nm (ϵ 15600); IR (CH_2Cl_2) 3620, 3450, 3040, 2940, 2830, 1635, 1430, 1340, 1280, 1020, 895, 795 cm^{-1}; mass spectrum (20 eV), m/e (relative intensity) 316 ($M^+ - H_2O$, 22), 298 (100), 280 (45), 253 (42); ^1H NMR 6.43 (dd, J = 15.1 , 11.0), 5.84 (d, J = 11.0), 5.82 (d, J = 15.1), 5.28 (d, J = 7), 4.93 (s), 4.85 (m), 4.75 (s), 4.66 (d, J = 14), 4.60 (d, J = 8), 4.29 (d, J = 14), 1.74 (br s, 3 H), 1.34 (s, 6 H).

Xeniaphyllenol (11). See ref 5.

4,5-Epoxyxeniaphyllenol (12): $[\alpha]^{25}_D$ +22° (*c* 1.1, $CHCl_3$); mp 69–71 °C. For all other data see ref 5.

Isoxeniaphyllenol (13): $[\alpha]^{25}_D$ −13° (*c* 0.5, $CHCl_3$); IR (neat) 3480, 3060, 2960, 2920, 2855, 1630, 1450, 1380, 1365, 1270, 1185, 1150, 970, 890 cm^{-1}; mass spectrum (20 eV), m/e (relative intensity) 288 (M^+, $C_{20}H_{32}O$, 1), 273 (2), 270 (7), 255 (6), 227 (7), 201 (7), 190 (9), 189 (59), 161 (23), 159 (27), 148 (55), 147 (67), 133 (99), 121 (99), 120 (99), 119 (100), 107 (99); ^1H NMR 5.62 (br s, 2 H), 5.29 (m), 4.94 (s), 4.83 (s), 1.60 (br s, 3 H), 1.32 (s, 6 H), 0.99 (s, 3 H).

4,5-Epoxyisoxeniaphyllenol (14): $[\alpha]^{25}_D$ +6° (*c* 1.6, $CHCl_3$); IR (neat) 3420, 3070, 2925, 2860, 1630, 1450, 1375, 1240, 1150, 975, 890, 865, 760 cm^{-1}; mass spectrum (20 eV), m/e (relative intensity) 304 (M^+, $C_{20}H_{32}O_2$, 1), 286 (2), 205 (4), 187 (6), 149 (13), 121 (33), 119 (97), 117 (100), 43 (47); ^1H NMR 5.60 (m, 2 H), 4.97 (s), 4.87 (s), 2.90 (dd, J = 10, 4), 2.64 (q, J = 9.4), 1.89 (t, J = 9.4), 1.30 (s, 6 H), 1.19 (s, 3 H), 1.03 (s, 3 H).

Xeniaphyllan-14,15-diol (15a): IR (neat) 3450, 3060, 2930, 2860, 1670, 1630, 1450, 1375, 1280, 1230, 1155, 1080, 950, 925, 890, 790, 760 cm^{-1}; mass spectrum (20 eV), m/e (relative intensity) 306 (M^+, $C_{20}H_{34}O_2$, 1.5), 291 (1), 288 (1), 270 (1), 247 (4), 189 (10), 161 (13), 148 (16), 135 (15), 133 (31), 121 (36), 119 (100), 117 (99.5), 107 (16), 93 (21), 81 (21), 71 (26); ^1H NMR 5.31 (m), 4.94 (s), 4.83 (s), 3.29 (dd, J = 10, 2), 1.61 (br s, 3 H), 1.21 (s, 3 H), 1.16 (s, 3 H), 0.99 (s, 3 H).

14-Acetoxyxeniaphyllandiol (15b): $[\alpha]^{25}_D$ −2° (*c* 1.7, $CHCl_3$); IR (neat) 3460, 3070, 2960, 2930, 2860, 1735, 1670, 1635, 1455, 1380, 1325, 1245, 1185, 1150, 1105, 1070, 1035, 985, 955, 885, 790, 765 cm^{-1}; mass spectrum (15 eV), m/e (relative intensity) 348 (M^+, $C_{22}H_{36}O_3$, 1.5), 330 (0.5), 288 (1), 273 (0.5), 270 (2), 189 (6), 148 (11), 133 (12), 121 (32), 119 (99), 117 (100); ^1H NMR 5.29 (m), 4.92 (s), 4.83 (s), 4.77 (dd, J = 10, 4), 2.12 (s, 3 H), 1.60 (br s, 3 H), 1.20 (s, 6 H), 0.98 (s, 3 H).

4,5-Epoxy-14-acetoxyxeniaphyllandiol (16): $[\alpha]^{25}_D$ +11° (*c* 1.6, $CHCl_3$); IR (neat) 3450, 3070, 2960, 2930, 2850, 1735, 1630, 1455, 1375, 1245, 1150, 1070, 1035, 960, 910, 860, 785, 765 cm^{-1}; mass spectrum (14 eV), m/e (relative intensity) 364 (M^+, $C_{22}H_{36}O_4$, 3), 347 (37), 346 (10), 304 (8), 287 (23), 286 (15), 205 (21), 201 (25), 187 (41), 164 (29), 152 (47), 147 (55), 108 (82), 106 (100); ^1H NMR 4.97 (s), 4.86 (s), 4.75 (dd, J = 10, 3), 2.88 (dd, J = 11, 4), 2.12 (s, 3 H), 1.18 (s, 9 H), 1.01 (s, 3H).

Acetylation of Xeniolide-B (7a) to 7b. Acetic anhydride (2 mL) was added to a solution of **7a** (150 mg) in pyridine (2 mL), and the reaction mixture was stirred at room temperature for 24 h. The excess reagents were then removed in vacuo, and the residue was chromatographed on a silica-H column. Elution with 1:9 ethyl acetate–CH_2Cl_2 gave compound **7b** (100 mg), identical in all respects (NMR, IR, TLC) with the natural material.

Acetylation of Triol 9a. Compound **9a** (55 mg) was acetylated with a Ac_2O–pyridine mixture, followed by the same workup as described for **7b**. Silica-H chromatography afforded, after elution with 1:9 ethyl acetate–CH_2Cl_2, diacetate **9b** as a viscous oil: IR (CH_2Cl_2) 3680, 3480, 2930, 2860, 1735, 1635, 1455, 1370, 1240, 1147, 1025, 860, 800 cm^{-1}; mass spectrum, m/e (relative intensity) 418 (M^+, $C_{24}H_{34}O_6$, could be seen only in chemical ionization mass spectroscopy), 400 (1), 358 (3), 340 (2), 300 (1), 299 (3), 298 (3), 251 (12), 171 (10), 145 (13), 122 (14), 108 (36), 94 (100), 69 (32), 55 (41); ^1H NMR 6.44 (dd, J = 15, 11), 5.89 (d, J = 11), 5.88 (d, J = 15), 5.68 (br t, J = 7–8), 5.49 (d, J = 8.2), 5.35 (br d, J = 7.6), 4.92 (s), 4.86 (s), 4.66 (d, J = 13.5), 4.37 (d, J = 13.5), 2.10 (s, 3 H), 2.03 (s, 3 H), 1.81 (br s, 3 H), 1.36 (s, 3 H), 1.25 (s, 3 H); ^{13}C NMR see Table V.

Oxidation of Triol 9a to Compound 7a. Compound **9a** (60 mg) was dissolved in acetone (2 mL) and added to freshly prepared Fetizon reagent (Ag_2CO_3 on Celite, 440 mg) in toluene (15 mL).[16] The reaction mixture was refluxed for 4.5 h, during which silver precipitated out on the flask walls. After the solid residue was filtered off, the solvents were removed in vacuo, and the mixture of the products was chromatographed to obtain a product (21 mg, 33%) identical in all respects with **7a**.

Epoxidation of Xeniaphyllenol (11) To Give Epoxide 12. To a solution of compound 11 (90 mg) in CH_2Cl_2 (15 mL) at 2 °C was added a solution of *m*-chloroperbenzoic acid (63 mg) in CH_2Cl_2 (5 mL) dropwise with stirring during a 1.5-h period. Stirring was continued for another 1 h. The excess of the peracid was removed with 10% Na_2CO_3 solution, and the solution was then washed with water, dried over $MgSO_4$, and evaporated to yield 85 mg of an oily material. After careful silica-H chromatography (elution with 5% ethyl acetate in CH_2Cl_2), two products were obtained. The main and more polar compound (67 mg) was a crystalline material, identical in all respects with the natural 4,5-epoxyxeniaphyllenol (**12**). The minor product (13 mg) was the 4,5-epoxy stereoisomer of **12**: IR (neat) 3450, 3070, 2940, 2860, 1635, 1480, 1385, 1070, 970, 890, 865, 760 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 304 (M^+, $C_{20}H_{32}O_2$, 0.5), 289 (4), 271 (8), 207 (9), 205 (9), 183 (13), 149 (18), 125 (20), 111 (29), 109 (42), 87 (100), 83 (35), 71 (50); ^1H NMR 5.20 (dt, J = 9, 1), 5.11 (s), 4.99 (s), 4.45 (dt, J = 9, 7), 2.99 (dd, J = 11, 2), 1.70 (br s, 6 H), 1.24 (s, 3 H), 1.03 (s, 3 H); ^{13}C NMR 152.9 (s), 134.4 (s), 129.1 (d), 112.3 (t), 65.9 (d), 63.9 (s), 61.0 (d), 53.3 (t), 51.1 (d), 47.6 (d), 41.9 (t), 36.5 (t), 36.3 (t), 35.0 (s), 29.5 (t), 28.1 (t) 25.7 (q), 22.6 (q), 19.5 (q), 18.2 (q).

Ph_3P/CCl_4 Isomerization of Alcohol 11. Compound 11 (70 mg) was refluxed for 24 h in CCl_4 (6 mL) in the presence of triphenylphosphine (250 mg) until no more starting material was detectable by TLC. After evaporation and silica gel column chromatography, two major products were obtained. The more polar one (eluted with 7:3 CH_2Cl_2–petroleum ether) was found to be isoxeniaphyllenol (**13**), identical in all respects with the natural material (35 mg). The second and nonpolar product, which was eluted with petroleum ether, is most likely the dehydration product of alcohol 11: 25 mg (ca. 70%); ^1H NMR (90 MHz) 6.17 (d, J = 16), 5.69 (dd, J = 16, 8), 5.33 (m), 4.96 (br s), 4.88 (br s, 3 H), 1.83 (br s, 3 H), 1.60 (br s, 3 H), 0.99 (s, 3 H); ^{13}C NMR 154.7, 142.1, 135.2, 134.8, 127.1, 124.5, 114.4, 112.0, 51.7, 48.5, 46.9, 39.8, 38.7, 36.5, 34.7, 28.5, 20.6, 18.8, 18.8, 16.4.

Basic Hydrolysis of Acetate 15b To Give 15a. To a solution of **15b** (59 mg) in methanol (3 mL) at 0 °C was added a 1% methanolic KOH solution (8 mL). The reaction mixture was allowed to stand at room temperature for 5 h, and then it was acidified with 10% acetic acid to pH 6.5. Most of the methanol was evaporated, the aqueous residue was extracted with $CHCl_3$ (3 × 15 mL), and the combined organic extracts were dried over $MgSO_4$ and evaporated to give diol **15a** (50 mg), identical in all respects with the natural material.

Acetylation of Diol 15a To Give 15b. Acetylation of diol **15a** (20 mg) with a few drops of acetic anhydride–pyridine solution, at room temperature, overnight, afforded after the usual workup a product indistinguishable from natural **15b**.

Microscale $NaIO_4$ Oxidation of Diol 15a To Give Aldehyde 22. To a solution of **15a** (5 mg) in 1:1 CH_3OH–H_2O (1 mL) was added a solution of $NaIO_4$ (30 mg) in CH_3OH–H_2O (4 mL), and the white emulsion was stirred for 3.5 h at room temperature. After evaporation of the methanol, the aqueous residue was extracted with $CHCl_3$, and the organic extract was dried and evaporated to give oily aldehyde **22**: 4 mg; ^1H NMR (60 MHz) 9.95 (t, J = 1.5).

Obscuronatin (23): UV end absorption; IR (neat) 3470, 2960, 2920, 2860, 1670, 1450, 1380, 1200, 1125, 1065, 1015, 982, 945, 910, 880, 860, 840, 790, 770 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 290 (M^+, $C_{20}H_{34}O$, 7), 275 (2.5), 272 (31), 192 (24), 191 (45), 190 (29), 187 (28), 161 (46), 159 (26), 135 (20), 121 (77), 119

(24), 109 (40), 108 (31), 107 (29), 105 (32), 95 (30), 93 (25), 82 (30), 81 (100), 69 (46), 43 (95); ^{1}H NMR 5.25–5.20 (m, 2 H), 5.05 (br t, J = 7), 4.99 (br d, J = 12), 1.68 (br s, 3 H), 1.58 (br s, 3 H), 1.53 (br s, 3 H), 1.18 (s, 3 H), 0.83 (d, J = 6.2); ^{13}C NMR 140.1 (d), 132.4 (s), 130.6 (s), 129.1 (d), 126.4 (d), 125.2 (d), 72.9 (s), 52.1 (d), 41.5 (t), 39.8 (t), 38.2 (t), 33.4 (t), 31.0 (q), 25.9 (d), 25.8 (q), 25.5 (t), 23.9 (t), 17.7 (q), 17.2 (q), 16.8 (q).

Microozonolysis of Obscuronatin (23). Ozone in oxygen was bubbled through a solution of compound **23** (10 mg) in ethyl acetate (3 mL) at −70 °C for 4 min. The ozonide was treated with excess of Ph_3P, and the reaction mixture was then warmed up to room temperature and immediately injected into a programmed gas chromatograph.[21] Comparison with fragment **24** obtained from trocheliophorol[22] on a 6 ft × $^1/_4$ in. i.d., 5% Carbowax on GCQ column (60–200 °C and 120–200 °C at 4 °C/min) confirmed the identity of the fragments. (The retention times of fragment **24** were 25.6 min in the first program and 15.9 min in the second one.)

Ph_3P/CCl_4 Dehydration of Alcohol 23 To Give Compounds 25 and 26. A solution of alcohol **23** (112 mg) and Ph_3P (250 mg) in CCl_4 (5 mL) was stirred at room temperature for 88 h. The solvent was then removed and the residue chromatographed on silica gel to give a 1:1 mixture of two isomeric nonpolar compounds (60 mg). This mixture was separated after extensive chromatography on 2% $AgNO_3$ impregenated silica gel columns to give two pure oily olefins **25** and **26**. Compound **25**: IR (CCl_4) 3080, 2960, 2920, 2860, 1645, 1450, 1380, 1280, 1245, 1220, 1165, 890, 720 cm^{-1}; mass spectrum (15 eV), m/e (relative intensity) 272 (M^+, $C_{20}H_{32}$, 86), 257 (4), 201 (8), 187 (100), 161 (54), 159 (24), 119 (38), 105 (60), 93 (36), 91 (42), 81 (50), 69 (76); ^{1}H NMR 5.53 (br s), 5.12 (br t, J = 7), 4.66 (s), 4.55 (s), 1.69 (br s, 6 H), 1.61 (br s, 3 H), 0.74 (d, J = 6.7, 3 H). Compound **26**: IR (CCl_4) 2960, 2920, 2860, 1645, 1450, 1380, 1240, 1180, 1160, 1075, 1010, 940, 910, 720 cm^{-1}; mass spectrum (15 eV), m/e (relative intensity) 272 (M^+, $C_{20}H_{32}$,85), 257 (10), 201 (8), 187 (100), 161 (94), 159 (86), 145 (22), 134 (83), 119 (50), 105 (88), 93 (26), 91 (45), 81 (59), 69 (66); ^{1}H NMR 5.41 (br s), 5.12 (br t, J = 7), 1.68 (br s, 9 H), 1.60 (br s, 3 H), 0.78 (d, J = 6.7, 3 H).

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Registry No. 1, 64504-52-5; 2, 68612-43-1; 3, 74175-94-3; 4, 74175-95-4; 5, 74175-96-5; 6, 70389-63-8; 7a, 70389-64-9; 7b, 74175-97-6; 8, 74175-98-7; 9a, 74175-99-8; 9b, 74176-00-4; 10a, 71117-53-8; 10b, 71093-24-8; 11, 68612-42-0; 12, 68612-41-9; 12 4,5-epoxy stereoisomer, 74219-32-2; 13, 68651-47-8; 14, 74176-01-5; 15a, 74176-02-6; 15b, 74176-03-7; 16, 74176-04-8; 17, 87-44-5; 18, 118-65-0; 19, 1139-30-6; 20, 60362-44-9; 21, 10306-22-6; 22, 74176-05-9; 23, 74176-06-0; 24, 68043-35-6; 25, 74219-33-3; 26, 74176-07-1.

Synthesis of Adamantane Derivatives. 50.[1] Facile Synthesis of 2,4-Oxa-Bridged Protoadamantanes and Their Conversions to 2-Substituted and 2,4-Disubstituted Protoadamantanes and a 2,4-Disubstituted Adamantane

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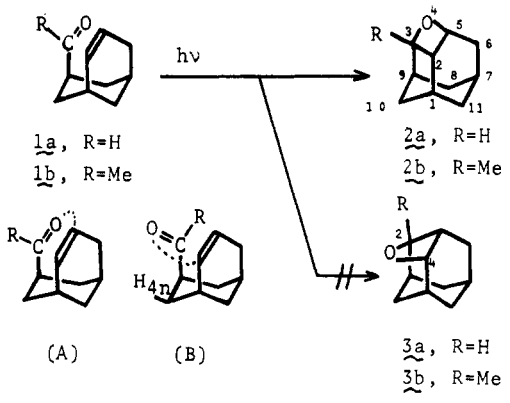
Intramolecular Paterno–Büchi reaction of 3-*endo*-acylbicyclo[3.3.1]non-6-enes **1a,b** proceeded regioselectively to afford exclusively 2,4-oxa-bridged protoadamantanes **2a,b** in good yields. The oxetane rings of **2a** and **2b** were cleaved by addition of hydrogen halides and by reduction with $LiAlH_4$, affording stereospecifically the corresponding 2,4-disubstituted and 2-substituted protoadamantane derivatives **7a, 7b, 9,** and **10**, respectively. Dehydration of 2-*exo*-methyl-2-*endo*-hydroxyprotoadamantane (**10**) with $POCl_3$–pyridine gave 2-methyleneprotoadamantane (**11**), while dehydration of the corresponding 4-*exo*-chloro derivative (**7b**) afforded exclusively 4(*e*)-chloro-2-methyleneadamantane (**14**) as a rearranged product in a high yield.

As an extension of our studies on the synthesis of 2,4-methanoadamantane and 2,4-methanoprotoadamantane,[2] we report in this paper a facile synthesis of 2,4-oxa-bridged protoadamantanes **2a** and **2b** via the intramolecular Paterno–Büchi reaction[3] as well as their conversions to some 2-substituted and 2,4-disubstituted protoadamantanes and a 2,4-disubstituted adamantane.

Results and Discussion

Intramolecular Paterno–Büchi Reaction of 3-*endo*-Acylbicyclo[3.3.1]non-6-enes. Irradiation of a 6.67 mM solution of 3-*endo*-formylbicyclo[3.3.1]non-6-ene (**1a**)[4] in deoxygenated *n*-hexane with a high-pressure mercury lamp (Vycor filter) led to a production of a new single sublimable product. Isolation of this product by chromatography on a silica gel column yielded 4-oxatetracyclo[5.3.1.0.^{2,5}0^{3,9}]undecane (**2a**; trivial 2,4-oxa-bridged

Scheme I



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