A New-Skeleton Diterpenoid, New Prenylbisabolanes, and Their Putative Biogenetic Precursor, from the Red Seaweed *Laurencia microcladia* from Il Rogiolo: Assigning the Absolute Configuration when Two Chiral Halves are Connected By Single Bonds

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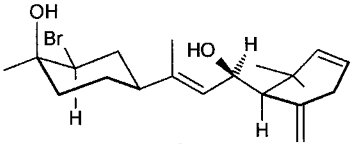
We report here a new-skeleton tricyclic diterpenoid, neorogioldiol (**8**), along with new prenylbisabolanes, rogioldiol D (**6**) and O^{11},15-cyclo-14-bromo-14,15-dihydrorogiol-3,11-diol (**5**), and their putative biogenetic precursor, (−)-geranyllinalool (**7**), isolated from the red seaweed *Laurencia microcladia*, which has colonized a small tract of the Tuscany coast called Il Rogiolo. In a case study of the assignment of the absolute configuration for molecules composed of chiral halves that are connected by single bonds, the absolute configuration of neorogioldiol (**8**) was based on *a*) the assumption of the identity of the cyclohexane moiety with co-occurring (2*S*,3*R*,6*S*)-rogiolal (**4**) and *b*) NMR-derived relative configurations for the bicyclic moiety, and *c*) the combination of these two pieces of information by molecular-mechanics-aided conformational analysis, in agreement with NOE data.

1. Introduction. – An atypical form of a red seaweed, *Laurencia microcladia* KÜTZNING (Ceramiales), which has colonized a short tract of the Tuscany coast called Il Rogiolo [1], is known as a prolific source of a variety of secondary metabolites. These include uniquely branched C_{15} acetogenins [1], novel chamigrane sesquiterpenes [2], obtusane diterpenes like rogioldiol A (**1**) [3], and 15,14-friedoobtusane diterpenes like rogioldiol B (**2**) and rogioldiol C (**3**) [4], besides rogiolal (**4**), which may be viewed as a degradation product of these diterpenes [3].



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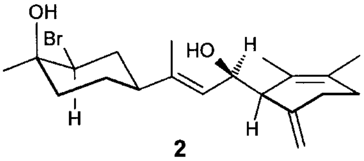

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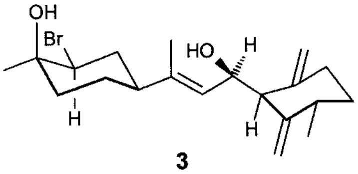

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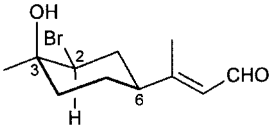

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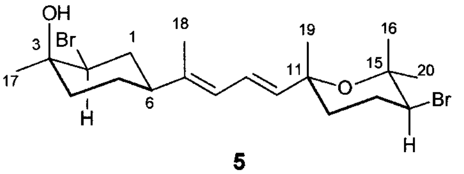
We have now isolated from this seaweed and report here a new-skeleton tricyclic diterpenoid, together with new prenylbisabolanes and the putative biogenetic precursor of all diterpenoids isolated from this seaweed. The new-skeleton diterpenoid is taken as a case study of the assignment of the absolute configuration from solution data of molecules composed of chiral halves connected by single bonds.

2. Results and Discussion. – 2.1. *Prenylbisabolanes* **5** *and* **6**. The composition $C_{20}H_{32}Br_2O_2$ for O^{11},15-cyclo-14-bromo-14,15-dihydrorogiol-3,11-diol (**5**) was deduced from MS and NMR data, which, revealing two olefinic bonds (*Exper. Part*), imply a bicyclic structure. That one must be a bromohydrin-bearing cyclohexane ring – as already found in compounds **1**–**3** from this seaweed – was inferred from ^{13}C- and ^{1}H-NMR data, which also support, in line with the UV absorption at λ_{max} 254 nm, the conjugated diene system.

The connection of the conjugated diene system of **5** to the tetrahydropyran ring rests on HMBC correlations for Me(19) (which was established to be bound to a quaternary C-atom): Me(19)/C(10), Me(19)/C(11), and Me(20)/C(14)[1]. The Br-atom was located at C(14) from δ(C(14)) 59.45 (*d*), heterocorrelated with δ(H) 4.08 (*dd*, *J* = 7.7 and 3.7 Hz), attributable to H–C(14). This coupling pattern suggests that the Br-atom undergoes a rapid exchange between the (equally populated) equatorial and axial positions because of a rapid inversion of the tetrahydropyran ring. Lowering the temperature did not allow detection of separate conformers: at – 60°, the coupling pattern for H–C(14) became a *dd* (*J* = 3.7 and 5.8 Hz), indicating a shift toward the conformation with the axial Br-atom. The (*E*,*E*) configuration finds evidence in a large coupling constant, *J*(9,10) = 15.6 Hz, strong NOEs H–C(8)/H–C(10) and Me(18)/H–C(9), and an upfield-located resonance at δ(C(18)) 14.97. The relative configurations rest on matching of the NMR data of compounds **1** [3] and **2**–**3** [4].

Because of the co-occurrence of compounds **1**–**4** and **5** in this seaweed, it is reasonable to assume that the 2,3-bromohydrin moiety in **5** has the same absolute configuration as rogiolal (**4**) [3]. However, the scarcity and instability of **5**, particularly on the silica gel used for chromatography, prevented us from assigning the configurations at C(11) and C(14), and thus, the enantiomeric form of the tetrahydropyran ring of **5** is equally possible.



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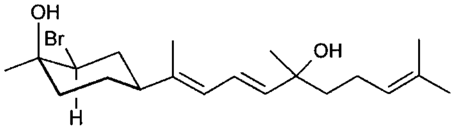

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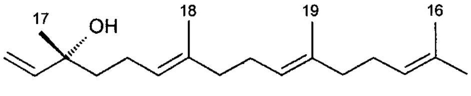

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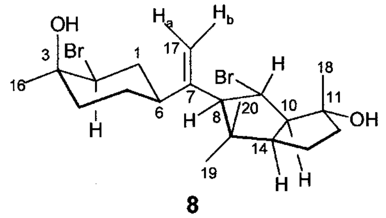

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A comparison of spectral data (*Exper. Part*) suggests that rogioldiol D (**6**) is the ring-opened form of O^{11},15-cyclo-14-bromo-14,15-dihydrorogiol-3,11-diol (**5**) (equivalent to the loss of a bromohydrin functionality from C(14)–C(15)).

MS, NMR, and chiroptical data for a further diterpene isolated from this seaweed (*Exper. Part*) fit nicely for (–)-geranyllinalool (**7**). This terpenoid was previously

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[1] Here and for all other compounds, arbitrary numbering of the backbone is used in line with previous work [3]; for systematic names, see *Exper. Part*.

isolated from oleoresins from the Norwegian spruce, *Picea abies*, and assigned (*R*) configuration at a good level of confidence by comparison of the molar optical rotation of its hydrogenation product with model compounds [5].

2.2. *Neorogiolane* **8**. MS and NMR data established the composition $C_{20}H_{32}Br_2O_2$ for neorogioldiol (**8**), which must be tricyclic to account for the presence of a single olefinic bond (*Table*). The presence of the 2,3-bromohydrin moiety was inferred, like for **5** and **6**, from matching the NMR data of rogioldiol A (**1**) [3], rogioldiol B (**2**), and rogioldiol C (**3**) [4].

Table 1. *^{1}H- and ^{13}C-NMR Data for Neorogioldiol* (**8**). δ in ppm rel. to $SiMe_4$, J in Hz.

	^{1}H-NMR		NOE (CDCl$_3$)	^{13}C-NMR (CDCl$_3$)
	CDCl$_3$ [a])	C$_6$D$_6$ [b])		
CH$_2$(1)	1.97 (*q*, $J = 12.6$, H$_{ax}$)	2.19 (*q*, $J = 12.4$, H$_{ax}$)	H$_a$–C(17)	40.44 (*t*)
	2.39 (*ddd*, $J = 2.7, 4.3, 12.6$, H$_{eq}$)	2.49 (*ddd*, $J = 12.4, 4.5, 2.6$, H$_{eq}$)		
H–C(2)	4.11 (*dd*, $J = 4.3, 12.6$)	3.73 (*dd*, $J = 12.5, 4.4$)	Me(16), H$_{eq}$–C(1)	65.80 (*d*)
C(3)	–	–		70.31 (*s*)
CH$_2$(4)	1.50 (br. *t*, $J = 13.3$, H$_{ax}$)	0.97 (br. *t*, $J = 13.3$, H$_{ax}$)	Me(16)	
	2.10 (*dt*, $J = 13.7, 2.7$, H$_{eq}$)	1.87 (*td*, $J = 3.0, 13.3$, H$_{eq}$)	Me(16)	37.56 (*t*)
CH$_2$(5)	1.85 (br. *q*, $J = 13.0$, H$_{ax}$)	1.95 (*dq*, $J = 3.8, 13.2$, H$_{ax}$)	H$_a$–C(17)	26.08 (*t*)
	1.50 (*ddd*, $J = 13.7, 3.0, 2.7$, H$_{eq}$)	1.37 (*ddd*, $J = 13.2, 3.3, 2.5$, H$_{eq}$)		
H–C(6)	1.76 (*tt*, $J = 12.6, 3.0$)	1.50 (*tt*, $J = 12.4, 3.3$)	Me(20)	46.53 (*d*)
C(7)	–	–		147.58 (*s*)
H–C(8)	2.48 (*d*, $J = 12.0$ [$J(8,9) = 11.9$])	2.30 (*d*, $J = 11.9$)	Me(19), H–C(6)	65.70 (*d*)
H–C(9)	3.74 (*dd*, $J = 12.0, 9.2$ [$J(9,10) = 9.2$])	3.60 (*dd*, $J = 11.9, 9.3$)	H$_b$–C(17), Me(18), Me(20)	54.32 (*d*)
H–C(10)	2.70 (*ddd*, $J = 12.5, 9.2, 1.4$ [$J(10,14) = 10.7$])	2.68 (br. *t*, $J = 10.6$)	H–C(14)	63.37 (*d*)
C(11)	–	–		80.55 (*s*)
CH$_2$(12)	1.45 (*m*)	1.21 (*dt*, $J = 12.4, 7.0$, H$_\beta$) 1.35 (*m*, H$_\alpha$)		23.68 (*t*)
CH$_2$(13)	1.78 (*ddd*, $J = 13.0, 9.5, 6.8$ [$J(13\beta,12\alpha = 0.8$, $J(13\beta,12\beta = 6.1$], H$_\beta$)	1.80 (*ddd*, $J = 12.7, 9.5, 6.8$, H$_\beta$)		
				41.71 (*t*)
	1.55 (*m*, [$J(13\alpha,12\alpha) = 6.8$, $J(13\alpha,12\beta) = 12.4$], H$_\alpha$)	1.34 (*m*, H$_\alpha$)		
H–C(14)	2.59 (*ddd*, $J = 12.5, 9.2, 2.1$ [$J(14.13\alpha) = 9.5$, $J(14,13\beta) = 1.7$])	2.39 (br. *t*, $J = 10.6$)	H–C(10), Me(19)	53.63 (*d*)
C(15)	–	–		41.71 (*s*)
Me(16)	1.32 (*s*)	1.12 (*s*)	H–C(2), H$_{ax}$–C(4)	30.51 (*q*)
CH$_2$(17)	5.21 (*s*, H$_a$)	5.13 (br. *s*, H$_a$)	H$_{ax}$–C(1), H$_{ax}$–C(5)	
	4.74 (*s*, H$_b$)	4.59 (br. *s*, H$_b$)	H–C(9), Me(20)	111.81 (*t*)
Me(18)	1.49 (*s*)	1.34 (*s*)	H–C(9)	24.33 (*q*)
Me(19)	1.02 (*s*)	0.79 (*s*)	Me(20), H–C(14), H–C(8)	31.27 (*q*)
Me(20)	0.66 (*s*)	0.45 (*s*)	Me(19), H–C(9), H$_b$–C(17)	19.87 (*q*)

[a]) ^3J Values in square brackets were calculated by *Altona*'s equation [6].

[b]) OH–C(3) at 1.66, and OH–C(11) at 0.66 ppm.

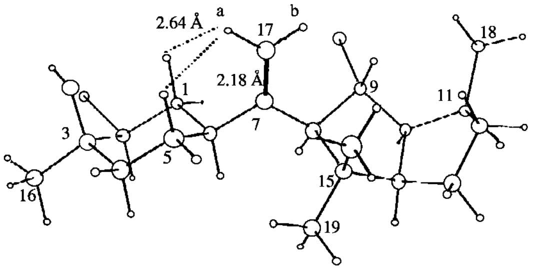

Figure. *MM-Calculated least-strain conformation of* **8**

The proton correlations within the segments C(8) to C(10) and C(12) to C(14) of **8** were deduced from selective decoupling and $^1H,^1H$-COSY experiments in C_6D_6 solution, where some key resonances are better separated than in $CDCl_3$ solution (*Table*). The corresponding ^{13}C-NMR resonances were assigned from HMQC experiments, showing the correlations H_a–C(17)/C(6), H_b–C(17)/C(8), Me(19)(or Me(20))/C(8), Me(19)(or Me(20))/C(14), Me(19) (or Me(20))/C(15), and Me(18)/C(10), Me(18)/C(11), and Me(18)/C(12). The relative configurations at the chiral centers in the bicyclic system are supported by both NOE enhancements and an excellent agreement of the observed ^3J coupling constants with those derived [6] from the MM-calculated least-strain conformation (*Table*). This conformer (*Fig.*) is less strained than the various conformers resulting from rotation around bonds C(6)–C(7) and C(7)–C(8) and is characterized by a plane containing the group C(7)=CH_2(17) in almost parallel fashion to the plane that contains the axial substituents for both the mono- and the bicyclic system. All observed NOE enhancements, including those above and those in the *Table*, between H–C(6) and H–C(8), are thus accounted for.

The way the configuration of the cyclohexane moiety in neorogioldiol (**8**) is linked to that for the bicyclic system, and the assumed absolute configuration for the cyclohexane moiety translated to the whole framework, warrants some comment. In fact, it is always difficult, in the absence of X-ray diffraction data, to assign the absolute configuration for systems composed of two configurationally defined halves connected by single bonds, like for **8**. Relative rotation of the two cyclic moieties in this compound is restrained, however, probably because of the allylic 1,2 strain that involves the exocyclic methylene unit. Models suggest that such strain can be relieved for small values of the dihedral angles H–C(6)–C(7)–C(8) and C(6)–C(7)–C(8)–H(8), thus allowing a quasi-eclipsing of H–C(6) to H–C(8). Repulsive *van der Waals* interactions of *a*) H_b–C(17) with both H_{ax}–C(9) and Me(20), *b*) H_{eq}–C(5) with Me(19), and *c*) Br–C(9) with H_{eq}–C(1) are relieved by the absolute configurations of the bicyclic ring. To minimize severe repulsive interactions of H_b–C(17) with Me(20) and Br–C(9) with H_{eq}–C(1), C(17) is tilted up by a small rotation of 30° – anticlockwise when looking toward C(7) from C(8) – around the C(7)–C(8) bond. Any strong repulsive interaction between Me(19) and H_{eq}–C(5) that may arise from this rotation is minimized by an equivalent rotation around the C(6)–C(7) bond in the opposite direction, *i.e.* clockwise on looking toward C(6) from C(7). This conformational assessment fits the NMR data, in particular NOE data. Thus, the molecular-mechanics(MM)-calculated distances in the minimized conformer (*Fig.*) between H_a–C(17) and either H_{ax}–C(1) or H_{ax}–C(5) differ sharply, 2.64 and 2.18 Å, respectively, in agreement with a NOE twice as large for H_a–C(17)/H_{ax}–C(5) as for H_a–C(17)/H_{ax}–C(1)²).

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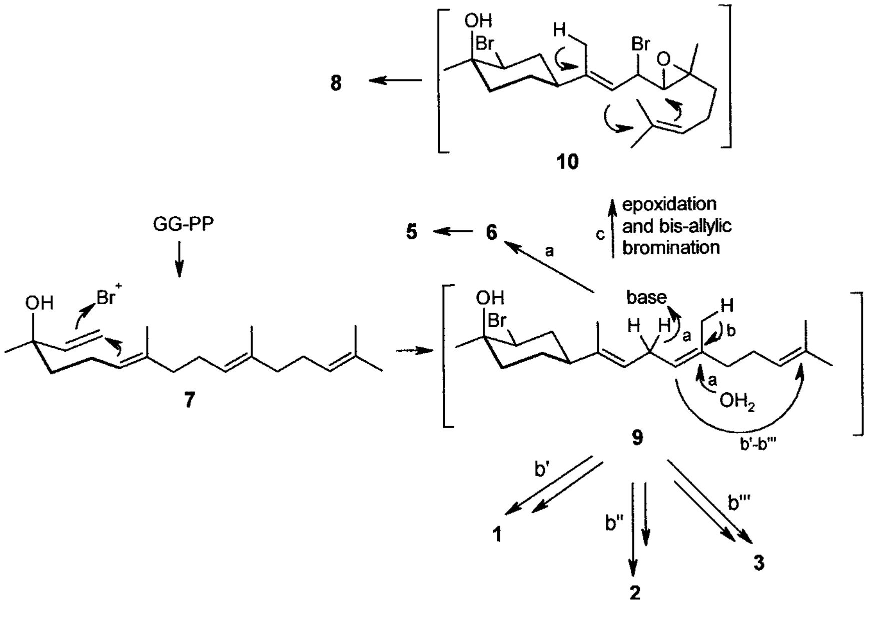
²) This refers to calculations by the MMX force field. MM Calculations by the MM3 force field emphasize these differences (3.21 and 2.11 Å, resp.).

A hypothetical diastereoisomer of **8** having a specular bicyclic moiety was ruled out from the specular conformation that it assumed according to MM calculations, with NOE values reversed for the two key proton couples $H_a-C(17)/H_{ax}-C(5)$ and $H_a-C(17)/H_{ax}-C(1)$, in contrast with the observed values. In conclusion, the observed NOEs allow transferring the biogenetically based assumption of a (2*S*,3*R*,6*S*) absolute configuration for the cyclohexane moiety [3] to the bicyclic moiety (8*R*,9*S*,10*R*,11*R*,14*R*)[3].

2.3. *The Biogenesis.* The diterpenoids described here fit a hypothetical unitary biogenetic *Scheme*, which also comprises all other diterpenoids previously isolated from the same seaweed [3][4]. In this hypothesis, geranylgeraniol pyrophosphate generated (−)-(*R*)-geranyllinalool (**7**) undergoes a bromoperoxidase-induced brominative cyclization to afford the elusive pivotal intermediate **9**. Rogioldiols A–C (**1**–**3**) [4] may arise from this intermediate, each pathway being triggered by a specific cyclase. Along another route, intermediate **9** may either undergo abstraction of the bis-allylic proton at C(9) by a basic enzyme active center, with concomitant hydroxylation at C(11), to give rogioldiol D (**6**) (from which O^{11},15-cyclo-14-bromo-14,15-dihydrorogiol-3,11-diol (**5**) may arise by intramolecular cyclization), or bromination followed by epoxidation at C(10)=C(11) to give intermediate **10**, along the pathway to neorogioldiol (**8**).

Although highly speculative, this *Scheme* fits all our observations and MM simulations. Any experimental verification of this proposal is left to biosynthetic experiments with the seaweed, perhaps with cell-free enzyme extracts. In any event, it is

Scheme. *Hypothetic Biogenetic Scheme for the Diterpenes Isolated from* Laurencia microcladia *of Il Rogiolo* (b′ = rogioldiol A cyclase; b″ = rogioldiol B cyclase; b‴ = rogioldiol C cyclase)



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[3] The case of **5** shows that there is no way to apply this methodology when exchange phenomena are fast on the NMR time scale and cannot be slowed down sufficiently by lowering the temperature.

curious that geranyllinalool, an often postulated precursor of diterpenes in terrestrial plants [5], where, however, it was rarely observed in either the levo- [5] or dextrorotatory form [7], occurs abundantly in a red seaweed, which is phylogenetically distant from higher plants. The most reasonable explanation is that terpenoids like **7** were unavoidable pivotal biosynthetic points during the evolution of terpene biosynthesis, and as such they may have arisen more than once.

We thank *A. Sterni* for recording the mass spectra and both *MURST* (Progetti di Interesse Nazionale) and *CNR*, Roma, for financial support.

Experimental Part

General. See [3]. Moreover, t_R in min. For compounds **5** and **8**, ^{1}H,^{1}H-COSY, 2D NOE, HMQC, and HMBC experiments were carried out. Differential 1D NOE is reported as irradiated H → observed H. Electrospray (EI) MS: *Esquire-Bruker* ion-trap instrument. MM Calculations were carried out by the GMMX and PCMODEL programs (based on the MMX force field) from *Serena Software*, Bloomington Indiana, and MM3(96) (based on the MM3 force field) from *QCPE*, Indiana University.

Isolation of Compounds. The residue (0.11 g) from evaporation of *Frs. 19–24*, out of the 54 fractions obtained before from *L. microcladia* extracts [8], was subjected to reversed-phase HPLC (gradient MeCN/H$_2$O) to give, from *Fr. 16*, pure **7** (t_R 15.6; 15.5 mg, 0.025%). The residue from *Fr. 10* (9 mg) was subjected to HPLC (*CN*, hexane/^{i}PrOH 97:3) yielding pure **6** (t_R 9.0; 1.5 mg, 0.002%). The residue (0.03 g) from *Fr. 9* gave *O^{11},15-cyclo-14-bromo-14,15-dihydrorogiol-3,11-diol* (**5**; t_R 11.4; 2.9 mg, 0.005%). The residue (0.178 g) from evaporation of *Frs. 37–43*, out of the 54 fractions above, was subjected to HPLC (*CN*, hexane/^{i}PrOH 95:5) to give the known diterpenoid obtusadiol, and degraded terpenoid rogiolal (**4**) and isorogiolal [3]. *Fr. 12* was further purified by reversed-phase HPLC (*RP-18*, MeCN/H$_2$O 7:3) to give pure neorogioldiol (**8**; t_R 14.4; 10.5 mg, 0.015%).

*O^{11},15-Cyclo-14-bromo-14,15-dihydrorogiol-3,11-diol (=(1*R*,2*S*,4*S*)-2-Bromo-4-{4-[(2*R**,5*S**)-5-bromo-2,6,6-trimethyl-2*H*-pyran-2-yl]-1-methylbuta-1,3-dienyl}-1-methylcyclohexanol*[4]; **5**). $[\alpha]_D^{20} = -33.3$ ($c = 0.20$, CCl$_4$). UV (MeOH): 245 (11700). ^{1}H-NMR (CDCl$_3$)[1]: 2.18 (*q*, $J = 12.3$, H$_{ax}$–C(1)); 2.07 (*m*, H$_{eq}$–C(1)); 4.16 (*dd*, $J = 4.7$, 12.3, H–C(2)); 2.11, 1.87 (2*m*, 2 H–C(4)); 1.70, 1.58 (2*m*, 2 H–C(5)); 1.99 (*tt*, $J = 3.4$, 12.3, H–C(6)); 5.81 (*qd*, $J = 1.0$, 10.9, H–C(8)); 6.26 (*dd*, $J = 10.9$, 15.6, H–C(9)); 5.62 (*d*, $J = 15.6$, H–C(10)); 1.89, 1.48 (2*m*, 2 H–C(12)); 2.25, 2.14 (2*m*, 2 H–C(13)); 4.08 (*dd*, $J = 3.7$, 7.7, H–C(14)); 1.34 (*s*, Me(16) or Me(20)); 1.32 (*s*, Me(17)); 1.72 (*d*, $J = 1.0$, Me(18)); 1.30 (*s*, Me(19)); 1.38 (*s*, Me(20) or Me(16)). NOE: 5.81 → 5.62, 1.99; 4.16 → 2.11, 2.00, 1.32; 1.72 → 6.26; 1.34 → 4.08; 1.32 → 4.16, 2.07; 1.30 → 5.62. ^{13}C-NMR (CDCl$_3$)[1]: 37.43 (*t*, C(1)); 65.76 (*d*, C(2)); 70.24 (*s*, C(3)); 38.77 (*t*, C(4)); 25.82 (*t*, C(5)); 48.54 (*d*, C(6)); 140.31 (*s*, C(7)); 123.77 (*d*, C(8)); 122.43 (*d*, C(9)); 140.60 (*d*, C(10)); 73.66 (*s*, C(11)); 32.50 (*t*, C(12)); 27.67 (*t*, C(13)); 59.45 (*d*, C(14)); 74.74 (*s*, C(15)); 29.36 (*q*, C(16)); 30.58 (*q*, C(17)); 14.93 (*q*, C(18)); 28.83 (*q*, C(19)); 28.79 (*q*, C(20)). EI-MS: 462, 464, 466 (2, 4, 2, $M^{+\bullet}$), 447, 449, 451 (6, 12, 6, $[M - \text{Me}]^+$), 382, 384 (1, 1, $[M - \text{HBr}]^{+\bullet}$), 367, 369 (5, 5, $[M - \text{Me} - \text{HBr}]^+$), 302 (4, $[M - 2\,\text{HBr}]^+$), 285, 287 (2, 2, $[M - \text{C}_7\text{H}_{12}\text{BrO}]^+$), 285, 287 (2, 2, $[M - \text{C}_7\text{H}_{12}\text{BrO}]^+$), 271, 273 (14, 14, $[M - \text{Me} - \text{C}_7\text{H}_{11}\text{BrO}]^{+\bullet}$), 218, 220 (15, 15), 175 (13), 159 (9), 145 (13), 133 (15), 129 (20), 119 (29), 111 (34), 107 (49), 93 (34), 69 (36), 55 (21), 43 (100). ESI-MS (MeCN/H$_2$O): 485, 487, 489 $[M + \text{Na}]^{+\bullet}$), 463, 465, 467 ($[M + \text{H}]^+$).

*Rogioldiol D (=(*1R,2S,4S*)-2-Bromo-4-(5-hydroxy-1,5,9-trimethyldeca-1,3,8-trienyl)-1-methylcyclohexanol*; **6**). ^{1}H-NMR (CDCl$_3$; only δs significantly different from those of **5**)[1]: 5.86 (*qd*, $J = 1.0$, 10.7, H–C(8)); 6.43 (*dd*, $J = 10.7$, 15.2, H–C(9)); 5.66 (*d*, $J = 15.2$, H–C(10)); 1.55 (*m*, 2 H–C(12)); 2.04 (*m*, 2 H–C(13)); 5.11 (br. *t*, 6.5, H–C(14)); 1.59 (*s*, Me(16)); 1.32 (*s*, Me(17)); 1.75 (*d*, $J = 1.0$, Me(18)); 1.29 (*s*, Me(19)); 1.67 (*s*, Me(20)). NOE: 5.86 → 5.66, 2.00; 4.16 → 2.11, 2.00, 1.32; 1.74 → 6.42; 1.66 → 5.11; 1.29 → 6.42; 1.32 → 4.16. ^{13}C-NMR (CDCl$_3$)[1]: 37.44 (*t*, C(1)); 65.81 (*d*, C(2)); 70.26 (*s*, C(3)); 38.75 (*t*, C(4)); 25.83 (*t*, C(5)); 48.54 (*d*, C(6)); 140.41 (*s*, C(7)); 123.53 (*d*, C(8)); 123.50 (*d*, C(9)); 139.01 (*d*, C(10)); 73.33 (*s*, C(11)); 42.52 (*t*, C(12)); 22.96 (*t*, C(13)); 124.34 (*d*, C(14)); 128.33 (*s*, C(15)); 25.72 (*q*, C(16)); 30.59 (*q*, C(17)); 14.92

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[4] The absolute configurations at the tetrahydropyran moiety are tentative.

(*q*, C(18)); 28.32 (*q*, C(19)); 17.74 (*q*, C(20)). EI-MS: 384, 386 (1, 1, $M^{+\cdot}$), 366, 368 (4, 4, $[M - H_2O]^{+\cdot}$), 323, 325 (7, 7), 286 (20, $[M - H_2O - HBr]^{\cdot+}$), 243 (15), 217 (14), 193 (42), 175 (52), 159 (22), 145 (29), 135 (52), 121 (28), 119 (41), 109 (50), 107 (70), 93 (73), 81 (61), 69 (92), 55 (36), 43 (100).

*(–)-(3*R*)-Geranyllinalool (=(3*R*)-3-Hydroxy-3,7,11,15-tetramethylhexadeca-1,6,10,14-tetraene*; **7**). $[\alpha]_D^{20} = -10.2$ ($c = 0.18$, CCl$_4$). ^{1}H-NMR (CDCl$_3$): 5.20 (*dd*, $J = 1.4$, 17.4, H$_a$–C(1)); 5.05 (*dd*, 1.4, 10.7, H$_b$–C(1)); 5.90 (*dd*, 10.7, 17.4, H–C(2)); 1.52 (*m*, 2 H–C(4)); 2.04 (*m*, 2 H–C(5), 2 H–C(8), 2 H–C(9), 2 H–C(12), 2 H–C(13)); 5.12 (br. *t*, $J = 6.5$, H–C(6)); 5.08 (br. *t*, $J = 6.5$, H–C(10), H–C(14)); 1.58 (br. *s*, Me(18), Me(19), Me(20)); 1.66 (br. *s*, Me(16)); 1.26 (*s*, Me(17)). ^{13}C-NMR (CDCl$_3$)1)): 111.65 (*t*, C(1)); 145.02 (*d*, C(2)); 73.47 (*s*, C(3)); 42.04 (*t*, C(4)); 22.69 (*t*, C(5)); 124.35 (*d*, C(6)); 135.58 (*s*, C(7)); 39.63 (*t*, C(8)); 26.72 (*t*, C(9)); 124.16 (*d*, C(10)); 135.02 (*s*, C(11)); 39.69 (*t*, C(12)); 26.52 (*t*, C(13)); 124.07 (*d*, C(14)); 131.24 (*s*, C(15)); 25.68 (*q*, C(16)); 27.87 (*q*, C(17)); 15.99, 16.02 (2*q*, C(18), C(19)); 17.67 (*q*, C(20)). EI-MS: 290 (1, $M^{+\cdot}$), 272 (2, $[M - H_2O]^{+\cdot}$), 257 (4, $[M - H_2O - Me]^{+}$), 204 (6, $[M - C_5H_{10}O]^{+\cdot}$), 189 (9), 175 (7), 161 (19), 147 (12), 136 (22), 133 (17), 123 (19), 121 (25), 119 (18), 109 (21), 107 (35), 105 (15), 95 (16), 93 (47), 91 (19), 81 (37), 79 (24), 69 (100), 55 (26), 43 (32), 41 (48).

*Neorogioldiol (=(1*R*,3a*R*,5*R*,6*S*,6a*R*)-6-Bromo-5-{1-[(1*S*,3*S*,4*R*)-3-bromo-4-hydroxy-4-methylcyclohexyl]ethenyl}octahydro-1,4,4-trimethylpentalen-1-ol*; **8**). $[\alpha]_D^{20} = -57$ ($c = 0.10$, CCl$_4$). NMR: *Table*. EI-MS: 462, 464, 466 (0.1, 0.2, 0.1, $M^{+\cdot}$), 382, 384 (17, 17, $[M - HBr]^{+\cdot}$), 365, 367 (10, 10, $[M - HBr - OH]^{+}$, 347, 349 (2, 2), 285 (12, $[365 (367) - HBr]^{+\cdot}$), 267 (5), 227 (10), 173 (6), 159 (8), 145 (7), 133 (13), 122 (100), 107 (19), 93 (20), 71 (21), 43 (75). HR-EI-MS: 382.1513 ± 0.005 ($C_{20}H_{31}BrO_2^{+}$; $[M - HBr]^{+\cdot}$; calc. 382.1507).

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