Diels–Alder Reaction of 2-Ethenyl-1,3,3-trimethylcyclohexene with 4*H*-Chromen-4-ones: A Convergent Approach to *ABCD* Tetracyclic Core of Marine Diterpenoids Related to Puupehenone and Kampanols

by **Rajesh M. Kamble** and **M. M. V. Ramana***

Department of Chemistry, University of Mumbai, Santacruz (East), Mumbai-400 098 India (phone: +91-9869074256; fax: +91-022-26528547; e-mail: mmvramana@yahoo.co.in)

A rapid assembly of the tetracyclic core of marine diterpenoids related to puupehenone and kampanols by *Diels–Alder* reaction of 2-ethenyl-1,3,3-trimethylcyclohexene with 4*H*-chromen-4-one (=4*H*-1-benzopyran-4-one) dienophiles is described.

Introduction. – The *Diels–Alder* reactions of 2-ethenyl-1,3,3-trimethylcyclohexene with dienophiles like dimethyl acetylenedicarboxylate [1], unsymmetrical 1,4-benzoquinones [2], 1,4-benzoquinone [3], substituted 1,4-benzoquinones [4], 2-(methoxycarbonyl)-4,4-dimethylcyclohex-2-enone [5], 3-[(*E*)-(methoxycarbonyl)prop-2-enoyl)-1,3-oxazolidin-2-one [6], acetylenedicarbaldehyde [7], (*S*)-5-(*tert*-Butyl)-3-hydroxy-2-isopropyl-1,4-benzoquinone [8], and conjugated ketones [9] have been reported. There are very few reports on [4+2] cycloaddition reactions using 4*H*-chromen-4-ones (=4*H*-1-benzopyran-4-ones) as dienophiles, and in all these cases an activating functionality like –CHO, –COR, –COOR, –CN, –Ar, *etc.* at C(3) have been utilized [10]. Only one *Diels–Alder* reaction of 2-ethenyl-1,3,3-trimethylcyclohexene with 6-bromo-3-cyano-4*H*-chromen-4-one has been reported [10a].

(+)-Puupehenone (**1**) [11a–11f], (+)-puupehedione (**2**) [11d], (−)-15-oxopuupehenol (**3**) [11e], (+)-15-cyanopuupehenone (**4**) [11d][11e], (−)-8-epichromazonarol (**5**) [12], (−)-15-cyanopuupehenol (**6**) [11e][13], chloropuupehenone (**7**) [11a], and cyclospongiaquinone-1 (**8**) [14] (*Fig. 1*) are an important group of biologically active marine terpenoids [15]. They are based on a mixed biogenetic origin involving a sesquiterpene unit with a quinol or quinone, and consist of a multiplicity of prenyl units uncommon in terrestrial organisms. They were isolated from sponges and possess a wide range of potent biological properties such as cytotoxic [11d][11e], antiviral [11d][11e], antimicrobial [11a], antifungal [11d], immunomodulatory [11d][11e], antitumor [11c][11h], antimalarial [11e], antibiotic [11i], antituberculosis [11j], antioxidant [11k], and insecticidal activities [11g]. The characteristic structural features, namely, a tetracyclic framework, four quaternary Me groups, a benzopyran ring, a trimethylcyclohexane moiety, four stereogenic centers at *AB* and *BC* ring junctions with *trans*- and *cis*-configuration, respectively, and an additional stereogenic center, *i.e.*, C(15) of ring *C*. These tetracyclic diterpenes and their biological activities attracted interest of chemists to develop strategies for their synthesis. Kampanols A–C (**9**–**11**, resp.; *Fig. 1*) are polycyclic natural products having structural features similar to

that of puupehenone. They were isolated from the fungal culture broth of *Stachybotrys kampalensis*, and they are novel and specific inhibitors of farnesyl-protein transferase [16].

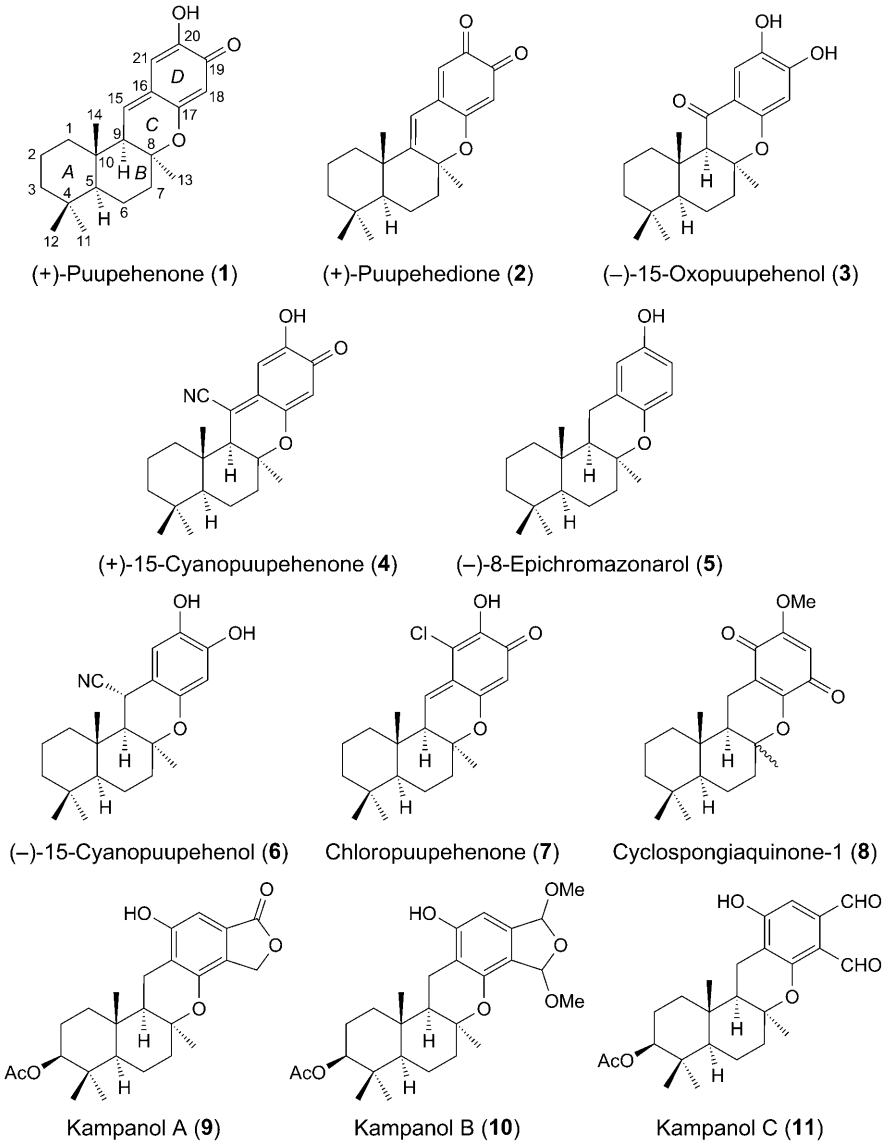


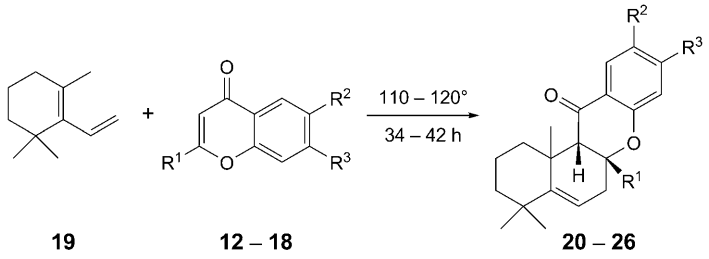
Fig. 1. *Puupehenone group of marine diterpenoids* **1**–**8** *and kampanols* **9**–**11**

Our interest in the synthesis of natural products [17] and absence of reports on *Diels–Alder* reaction of 2-ethenyl-1,3,3-trimethylcyclohexene with 4*H*-chromen-4-ones without an activating group at C(2)=C(3) led us to explore the synthetic potential

of 4*H*-chromen-4-ones such as 6,7-dimethoxy-2-methyl-4*H*-chromen-4-one (**12**) [18], 6-methoxy-2-methyl-4*H*-chromen-4-one (**13**) [19], 2-methyl-6,7-(methylenedioxy)-4*H*-chromen-4-one (**14**) [20], 2-methyl-6-nitro-4*H*-chromen-4-one (**15**) [21], 2-methyl-4*H*-chromen-4-one (**16**) [22], flavone (**17**) [23], and 4*H*-chromen-4-one (**18**) [24] as dienophiles in [4 + 2] cycloaddition reactions. We envisaged that, when the diene 2-ethenyl-1,3,3-trimethylcyclohexene (**19**) [1b] could be used, then such a cycloaddition would lead to a convergent approach for the construction of the tetracyclic core of puupehenone and kampanol analogues.

Results and Discussion. – Here are the results (*Scheme*). The reaction of **12** with **19** proceeded at 120° in a sealed tube for 40 h to give the cycloadduct **20** in a moderate yield. The reaction was found to be regioselective as indicated by ^{1}H-NMR data, which exhibited a *singlet* at δ(H) 2.71 for H–C(12a) whereas the H–C(6a) signal was absent. The signals of the diastereotopic H-atoms at C(1) appeared at δ(H) 2.18 and 1.65. These data indicate the formation of the regioisomer **20**[1]) (*Fig. 2*).

Scheme. *Synthesis of Tetracyclic Compounds* **20** – **26**



19 **12 – 18** **20 – 26**

The reaction was also stereoselective as indicated by a *singlet* for Me–C(6a) at δ(H) 1.39 and at δ(H) 1.21 for Me–C(12b). The corresponding C-signals appeared at δ(C) 34.2 (*Me*–C(6a)) and δ(C) 23.8 (*Me*–C(12b)).

These high δ values suggest the formation of the *endo*-configured product (*Fig. 2*). Recently, *Wallace* and co-workers [25] reported the synthesis of the (±)-*exo*-1,2,3,4,6,6a,12a,12b-octahydro-9,10-dimethoxy-4,4,6a,12b-tetramethylbenzo[*a*]xanthen-12-one, which exhibited lower δ values in the ^{1}H-NMR spectrum for the H-atoms at C(12a), and of Me–C(6a) and Me–C(12b). Furthermore this compound has a melting point of 165°, whereas **20** melts at 102°. Moreover, (±)-*exo*-1,2,3,4,6,6a,12a,12b-octahydro-4,4,6a,12b-tetramethylbenzo[*a*]xanthen-12-one is an oil [25], but our **24** is a solid with a melting point of 60°. The corresponding spectrum of **24** also displayed higher δ values for H–C(12a), and Me–C(6a) and Me–C(12b). All these evidences suggest the formation of the *endo*-product. This represents the first example of a highly stereoselective [4 + 2] cycloaddition reaction involving easily available 4*H*-chromen-4-one dienophiles.

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[1]) The ball-and-stick models were generated by using Materials Studio v4.4.0.0030, *Accelrys Software Inc.*

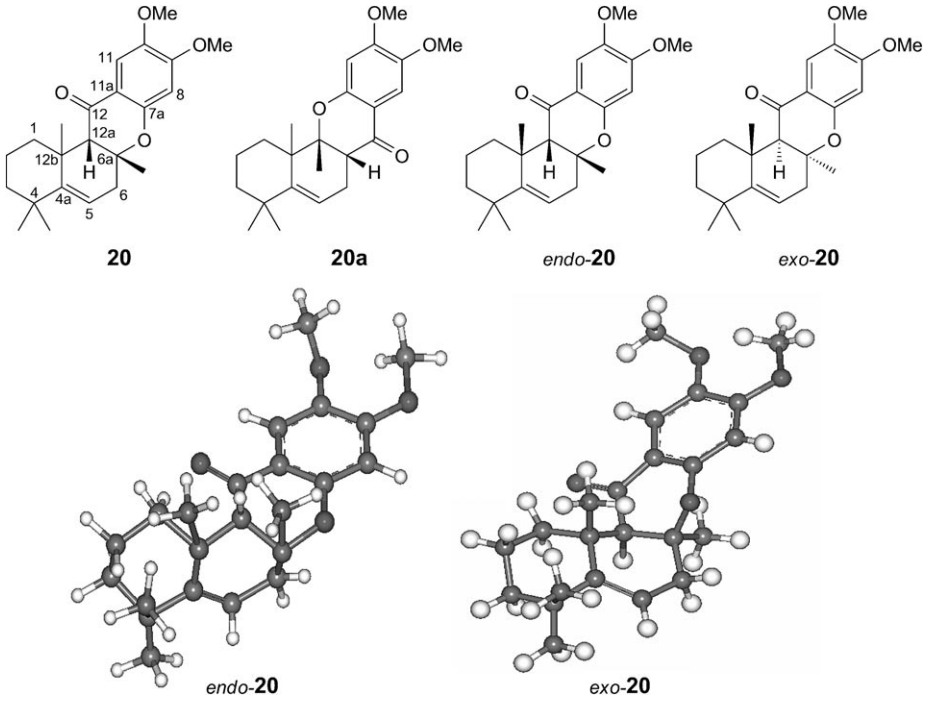

Fig. 2. *Regioisomers* **20** *and* **20a**, endo- *and* exo-*conformations, and ball-and-stick models of* **20**

Similar results were obtained with the other 4*H*-chromen-4-ones **13**–**18** (*Table*). In all these cases, the formation of the tetracyclic core as in puupehenone (**1**) and related marine terpenoids and kampanols was observed. Further, the catalytic hydrogenation of the C(4a)=C(5) bond could lead to a *trans*-fused *AB* ring [3][4], which is present in these natural products.

Table. *Reaction of 2-Ethenyl-1,3,3-trimethylcyclohexene* (**19**) *with 4*H*-Chromen-4-ones* **12**–**18**.

Entry	4*H*-Chromen-4-one	R^1	R^2	R^3	Product	Temp [°]	Time [h]	Yield[a]) [%]
1	**12**	Me	MeO	MeO	**20**	120	40	37
2	**13**	Me	MeO	H	**21**	120	40	37
3	**14**	Me	–OCH_2O–		**22**	120	42	36
4	**15**	Me	NO_2	H	**23**	120	40	32
5	**16**	Me	H	H	**24**	110	34	35
6	**17**	Ph	H	H	**25**	110	38	34
7	**18**	H	H	H	**26**	110	38	38

[a]) Yield of isolated product.

In conclusion, we have accomplished the first highly stereoselective [4 + 2] cycloaddition reaction using 4*H*-chromen-4-ones as dienophiles and thereby demonstrated the potential of this reaction in constructing the tetracyclic core of the marine

diterpenoids related to puupehenone analogues **1**–**8** and kampanols **9**–**11** in a convergent manner.

Experimental Part

General. The b.p. of petroleum ether (PE) used was in the range of 60–80°. Column chromatography (CC): silica gel (SiO_2, 60–120 mesh; *S.D. Fine Chemicals Ltd.*). M.p.: *EXPO HI-TECH* Melting-point apparatus; uncorrected. UV Spectra: *Shimadzu* UV/VIS Spectrophotometer *UV-2401PC* using MeOH as solvent, λ_{max} in nm (ε). IR Spectra: *Perkin-Elmer Spectrum One* FT-IR Spectrophotometer in KBr. ^{1}H- and ^{13}C-NMR spectra: *Bruker AVANCE* (^{1}H: 300; ^{13}C: 75 MHz) spectrometer in $CDCl_3$ and with TMS as an internal standard, δ in ppm and coupling constants J in Hz. EI-MS: *3200 Q TRAP* LC-MS-MS System *MDS SCI EX SHIMADZU PROMINANCE LC* and *Varian 500-MS* (*Model 210*) LC-MS IT Mass spectrometer (at 70 eV, *m*/*z* (rel-%)). Elemental analyses: *Euro-Vector EA 3000* elemental analyzer.

General Procedure (*GP*) *for Preparation of* **20**–**26**. A mixture of *2-ethenyl-1,3,3-trimethylcyclohexene* (**19**; 900 mg, 6 mmol) and **12**–**18** (0.6 mmol) in a sealed glass tube was heated in an oil bath (*Table*). The thus obtained light brown semisolid product was purified by CC to yield **20**–**26**.

rel-*(6a*R*,12a*S*,12b*R*)-1,2,3,4,6,6a,12a,12b-Octahydro-9,10-dimethoxy-4,4,6a,12b-tetramethyl-12*H*-benzo[*a*]xanthen-12-one* (**20**). CC (PE/$CHCl_3$ 3:7) gave **20** (49 mg, 37%). Colorless solid. M.p. 102°. UV/VIS: 339 (2822), 275 (4235), 236 (5757), 211 (5486). IR: 2924, 1678 (C=O), 1474, 1266, 1063. ^{1}H-NMR ($CDCl_3$): 7.14 (*s*, H–C(11)); 7.01 (*s*, H–C(8)); 5.58 (*t*, J = 3.9, H–C(5)); 3.90 (*s*, MeO); 3.86 (*s*, MeO); 2.71 (*s*, H–C(12a)); 2.61 (*dd*, J = 9.0, 18.0, H–C(6)); 2.53 (*dd*, J = 9.0, 18.0, H–C(6)); 2.18–1.65 (*m*, CH_2(1)); 1.72–1.61 (*m*, CH_2(2)); 1.43–1.18 (*m*, CH_2(3)); 1.39 (*s*, Me–C(6a)); 1.21 (*s*, Me–C(12b)); 1.13 (*s*, Me_{eq}–C(4)); 1.11 (*s*, Me_{ax}–C(4)). ^{13}C-NMR ($CDCl_3$): 199.5 (C=O); 155.2 (C(9)); 154.4 (C(7a)); 154.2 (C(10)); 140.8 (C(4a)); 137.3 (C(11a)); 132.1 (C(11)); 130.5 (C(8)); 121.2 (C(5)); 78.6 (C(6a)); 64.2 (C(12a)); 56.6 (MeO); 56.2 (MeO); 37.5 (C(1)); 37.1 (C(12b)); 34.2 (Me(6a)); 33.5 (Me_{eq}(4)); 32.6 (C(4)); 32.0 (C(6)); 23.8 (Me(12b)); 22.7 (Me_{ax}(4)); 20.6 (C(3)); 17.5 (C(2)). MS: 370 (11, M^+). Anal. calc. for $C_{23}H_{30}O_4$: C 74.59, H 8.10; found: C 74.83, H 8.03.

rel-*(6a*R*,12a*S*,12b*R*)-1,2,3,4,6,6a,12a,12b-Octahydro-10-methoxy-4,4,6a,12b-tetramethyl-12*H*-benzo[*a*]xanthen-12-one* (**21**). CC ($CHCl_3$) gave **21** (42 mg, 37%). Colorless solid. M.p. 111°. UV/VIS: 321 (3856), 229 (11487). IR: 3061, 2924, 1676 (C=O), 1483, 1239, 1028. ^{1}H-NMR ($CDCl_3$): 7.19 (*s*, H–C(11)); 7.09 (*d*, J = 8.9, H–C(9)); 6.99 (*d*, J = 8.9, H–C(8)); 5.59 (*t*, J = 3.8, H–C(5)); 3.88 (*s*, MeO); 2.80 (*s*, H–C(12a)); 2.59 (*dd*, J = 9.0, 18.1, H–C(6)); 2.51 (*dd*, J = 9.0, 18.1, H–C(6)); 2.16–1.64 (*m*, CH_2(1)); 1.71–1.60 (*m*, CH_2(2)); 1.42–1.19 (*m*, CH_2(3)); 1.38 (*s*, Me–C(6a)); 1.22 (*s*, Me–C(12b)); 1.14 (*s*, Me_{eq}–C(4)); 1.12 (*s*, Me_{ax}–C(4)). ^{13}C-NMR ($CDCl_3$): 199.1 (C=O); 154.1 (C(7a)); 153.2 (C(10)); 141.2 (C(4a)); 137.5 (C(11a)); 131.7 (C(11)); 130.9 (C(9)); 126.2 (C(8)); 121.0 (C(5)); 78.3 (C(6a)); 64.1 (C(12a)); 55.9 (MeO); 37.2 (C(12b)); 36.9 (C(1)); 33.9 (Me(6a)); 32.8 (Me_{eq}(4)); 32.2 (C(4)); 31.8 (C(6)); 23.2 (Me(12b)); 22.4 (Me_{ax}(4)); 20.4 (C(3)); 18.0 (C(2)). MS: 340 (5, M^+), 191 (100), 149 (17), 135 (18). Anal. calc. for $C_{22}H_{28}O_3$: C 77.64, H 8.23; found: C 77.43, H 8.33.

*6-Methyl-8*H*-[1,3]dioxolo[4,5-*g*]chromen-8-one* (**14**). This compound was prepared by utilizing the general procedure reported for synthesis of chromone in [20]. CC (PE/$CHCl_3$ 5:5) gave **14** (615 mg, 98%). Faint yellow crystals. M.p. 101–102°. UV/VIS: 347 (3881), 276 (3303), 238 (6472), 212 (5653). IR: 2922, 1632 (C=O), 1484, 1035, 922. ^{1}H-NMR ($CDCl_3$): 7.27 (*s*, 1 H); 7.05 (*s*, 1 H); 6.44 (*s*, 2 H); 5.98 (*s*, 1 H); 2.52 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 201.9 (C=O); 155.2; 154.9; 154.4; 140.4; 138.1; 132.3; 129.8; 128.4; 101.7; 26.4. MS: 204 (21, M^+), 148 (54), 118 (83), 116 (100). Anal. calc. for $C_{11}H_8O_4$: C 64.70, H 3.92; found: C 64.50, H 3.99.

rel-*(6a*R*,13a*S*,13b*R*)-1,2,3,4,6,6a,13a,13b-Octahydro-4,4,6a,13b-tetramethyl-13*H*-benzo[*a*][1,3]dioxolo[4,5-*i*]xanthen-13-one* (**22**). CC (PE/$CHCl_3$ 7:3) gave **22** (44 mg, 36%). Colorless solid. M.p. 98°. UV/VIS: 347 (3945), 276 (3386), 239 (7085), 210 (6929). IR: 2924, 1680 (C=O), 1484, 1035, 923. ^{1}H-NMR ($CDCl_3$): 7.10 (*s*, H–C(11)); 7.03 (*s*, H–C(8)); 5.97 (*s*, OCH_2O); 5.60 (*t*, J = 3.9, H–C(5)); 2.69 (*s*, H–C(12a)); 2.64 (*dd*, J = 9.2, 18.2, H–C(6)); 2.55 (*dd*, J = 9.2, 18.2, H–C(6)); 2.19–1.67 (*m*, CH_2(1)); 1.69–1.62 (*m*, CH_2(2)); 1.42–1.18 (*m*, CH_2(3)); 1.39 (*s*, Me–C(6a)); 1.20 (*s*, Me–C(12b)); 1.15 (*s*,

Me_{eq}–C(4)); 1.13 (*s*, Me_{ax}–C(4)). ^{13}C-NMR ($CDCl_3$): 199.4 (C=O); 154.8 (C(9)); 154.5 (C(7a)); 154.1 (C(10)); 140.5 (C(4a)); 137.5 (C(11a)); 132.5 (C(11)); 130.2 (C(8)); 121.4 (C(5)); 101.1 (OCH_2O); 78.7 (C(6a)); 63.8 (C(12a)); 37.5 (C(12b)); 37.2 (C(1)); 34.1 (Me(6a)); 32.9 (Me_{eq}(4)); 32.5 (C(4)); 32.2 (C(6)); 23.5 (Me(12b)); 22.8 (Me_{ax}(4)); 20.5 (C(3)); 17.8 (C(2)). MS: 354 (4, M^+), 352 (100), 236 (10), 220 (40), 205 (21). Anal. calc. for $C_{22}H_{26}O_4$: C 74.57, H 7.34; found: C 74.83, H 7.46.

rel-*(6a*R*,12a*S*,12b*R*)-1,2,3,4,6,6a,12a,12b-Octahydro-4,4,6a,12b-tetramethyl-10-nitro-12*H*-benzo[*a*]xanthen-12-one* (**23**). CC ($CHCl_3$) gave **23** (40 mg, 32%). Colorless solid. M.p. 171°. UV/VIS: 296 (4131), 239 (10304). IR: 3063, 2925, 1679 (C=O), 1531, 1467. ^{1}H-NMR ($CDCl_3$): 9.03 (*s*, H–C(11)); 8.46 (*d*, *J* = 9.2, H–C(9)); 7.54 (*d*, *J* = 9.2, H–C(8)); 5.55 (*t*, *J* = 3.9, H–C(5)); 2.78 (*s*, H–C(12a)); 2.62 (*dd*, *J* = 8.9, 18.0, H–C(6)); 2.54 (*dd*, *J* = 8.9, 18.0, H–C(6)); 2.20–1.68 (*m*, CH_2(1)); 1.71–1.64 (*m*, CH_2(2)); 1.42–1.19 (*m*, CH_2(3)); 1.39 (*s*, Me–C(6a); 1.24 (*s*, Me–C(12b)); 1.16 (*s*, Me_{eq}–C(4)); 1.13 (*s*, Me_{ax}–C(4)). ^{13}C-NMR ($CDCl_3$): 199.8 (C=O); 159.2 (C(10)); 154.8 (C(7a)); 148.5 (C(11)); 144.6 (C(9)); 140.4 (C(4a)); 138.1 (C(11a)); 127.8 (C(8)); 120.5 (C(5)); 78.5 (C(6a)); 64.1 (C(12a)); 37.5 (C(12b)); 37.1 (C(1)); 34.3 (Me(6a)); 33.7 (Me_{eq}(4)); 32.7 (C(4)); 31.7 (C(6)); 23.1 (Me(12b)); 22.3 (Me_{ax}(4)); 20.8 (C(3)); 17.7 (C(2)). MS: 355 (8, M^+), 327 (23), 206 (100), 160 (31), 143 (10). Anal. calc. for $C_{21}H_{25}NO_4$: C 70.98, H 7.04, N 3.94; found: C 70.72, H 6.92, N 4.06.

rel-*(6a*R*,12a*S*,12b*R*)-1,2,3,4,6,6a,12a,12b-Octahydro-4,4,6a,12b-tetramethyl-12*H*-benzo[*a*]xanthen-12-one* (**24**). CC ($CHCl_3$) gave **24** (56 mg, 35%). Colorless solid. M.p. 60°. UV/VIS: 295 (2551), 222 (7003). IR: 1676 (C=O), 1478. ^{1}H-NMR ($CDCl_3$): 7.04 (*d*, *J* = 8.5, H–C(11)); 6.97 (*d*, *J* = 8.5, H–C(8)); 6.93 (*t*, *J* = 8.6, H–C(9)); 6.90 (*t*, *J* = 8.5, H–C(10)); 5.58 (*t*, *J* = 3.7, H–C(5)); 2.75 (*s*, H–C(12a)); 2.60 (*dd*, *J* = 9.1, 18.1, H–C(6)); 2.52 (*dd*, *J* = 9.1, 18.1, H–C(6)); 2.19–1.66 (*m*, CH_2(1)); 1.69–1.60 (*m*, CH_2(2)); 1.44–1.17 (*m*, CH_2(3)); 1.39 (*s*, Me–C(6a)); 1.23 (*s*, Me–C(12b)); 1.13 (*s*, Me_{eq}–C(4)); 1.10 (*s*, Me_{ax}–C(4)). ^{13}C-NMR ($CDCl_3$): 199.2 (C=O); 155.1 (C(7a)); 140.1 (C(4a)); 137.7 (C(11a)); 128.2 (C(11)); 126.5 (C(8)); 121.4 (C(9)); 121.2 (C(10)); 120.8 (C(5)); 78.2 (C(6a)); 64.5 (C(12a)); 37.2 (C(12b)); 37.4 (C(1)); 34.0 (Me(6a)); 33.4 (Me_{eq}(4)); 32.4 (C(6)); 32.2 (C(4)); 23.5 (Me(12b)); 21.9 (Me_{ax}(4)); 21.0 (C(3)); 17.4 (C(2)). MS: 310 (4, M^+), 191 (100), 161 (96). Anal. calc. for $C_{21}H_{26}O_2$: C 81.29, H 8.38; found: C 81.03, H 8.50.

rel-*(6a*R*,12a*S*,12b*R*)-1,2,3,4,6,6a,12a,12b-Octahydro-4,4,12b-trimethyl-6a-phenyl-12*H*-benzo[*a*]xanthen-12-one* (**25**). CC ($CHCl_3$) gave **25** (45 mg, 34%). Colorless solid. M.p. 105–106°. UV/VIS: 294 (4845), 250 (4076), 20 (4965). IR: 3070, 2924, 1678 (C=O), 1495. ^{1}H-NMR ($CDCl_3$): 6.83–7.10 (*m*, 9 arom. H); 5.73 (*t*, *J* = 3.8, H–C(5)); 2.91 (*s*, H–C(12a)); 2.63 (*dd*, *J* = 9.0, 18.1, H–C(6)); 2.56 (*dd*, *J* = 9.0, 18.1, H–C(6)); 2.20–1.66 (*m*, CH_2(1)); 1.69–1.60 (*m*, CH_2(2)); 1.40–1.19 (*m*, CH_2(3)); 1.24 (*s*, Me–C(12b)); 1.16 (*s*, Me_{eq}–C(4)); 1.14 (*s*, Me_{ax}–C(4)). ^{13}C-NMR ($CDCl_3$): 199.1 (C=O); 155.5 (C(7a)); 140.9 (C(4a)); 137.3 (C(11a)); 128.5 (C(11)); 126.4 (C(8)); 127.3; 122.8; 122.8; 121.7 (C(5)); 121.1 (C(9)); 120.8 (C(10)); 119.8; 119.8; 115.5; 80.4 (C(6a)); 66.5 (C(12a)); 37.5 (C(12b)); 37.2 (C(1)); 33.2 (Me_{eq}(4)); 32.1 (C(4)); 31.2 (C(6)); 24.0 (Me(12b)); 22.4 (Me_{ax}(4)); 20.9 (C(3)); 17.5 (C(2)). MS: 372 (8, M^+); 344 (48), 223 (100), 121 (58), 77 (11). Anal. calc. for $C_{26}H_{28}O_2$: C 83.87, H 7.52; found: C 84.13, H 7.64.

rel-*(6a*R*,12a*S*,12b*R*)-1,2,3,4,6,6a,12a,12b-Octahydro-4,4,12b-trimethyl-12*H*-benzo[*a*]xanthen-12-one* (**26**). CC ($CHCl_3$) gave **26** (45 mg, 38%). Colorless solid. M.p. 55°. UV/VIS: 296 (3267), 238 (4609), 219 (7800). IR: 3085, 2925, 1677 (C=O), 1474. ^{1}H-NMR ($CDCl_3$): 7.03 (*d*, *J* = 5.0, H–C(11)); 6.99 (*d*, *J* = 5.0, H–C(8)); 6.92 (*t*, *J* = 5.2, H–C(9)); 6.89 (*t*, *J* = 5.1, H–C(10)); 5.56 (*t*, *J* = 3.9, H–C(5)); 3.43 (*ddd*, *J* = 5.2, 8.9, H–C(6a)); 2.79 (*d*, *J* = 4.8, H–C(12a)); 2.41 (*ddd*, *J* = 5.2, 8.9, H–C(6)); 2.20 (*ddd*, *J* = 5.2, 8.9, H–C(6)); 2.16–1.68 (*m*, CH_2(1)); 1.71–1.63 (*m*, CH_2(2)); 1.42–1.18 (*m*, CH_2(3)); 1.22 (*s*, Me–C(12b)); 1.15 (*s*, Me_{eq}–C(4)); 1.12 (*s*, Me_{ax}–C(4)). ^{13}C-NMR ($CDCl_3$): 199.4 (C=O); 155.2 (C(7a)); 140.2 (C(4a)); 137.2 (C(11a)); 128.3 (C(11)); 126.2 (C(8)); 121.5 (C(5)); 121.2 (C(9)); 120.9 (C(10)); 79.2 (C(6a)); 63.8 (C(12a)); 37.2 (C(12b)); 36.8 (C(1)); 33.8 (Me_{eq}(4)); 32.7 (C(4)); 31.5 (C(6)); 23.9 (Me(12b)); 22.1 (Me_{ax}(4)); 21.1 (C(3)); 17.2 (C(2)). MS: 296 (12, M^+), 147 (100), 105 (12), 91 (58), 77 (72). Anal. calc. for $C_{20}H_{24}O_2$: C 81.08, H 8.10; found: C 81.34, H 8.22.

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