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1,9-DIDEOXYFORSKOLIN. ENOLATE FORMATION - OXIDATION

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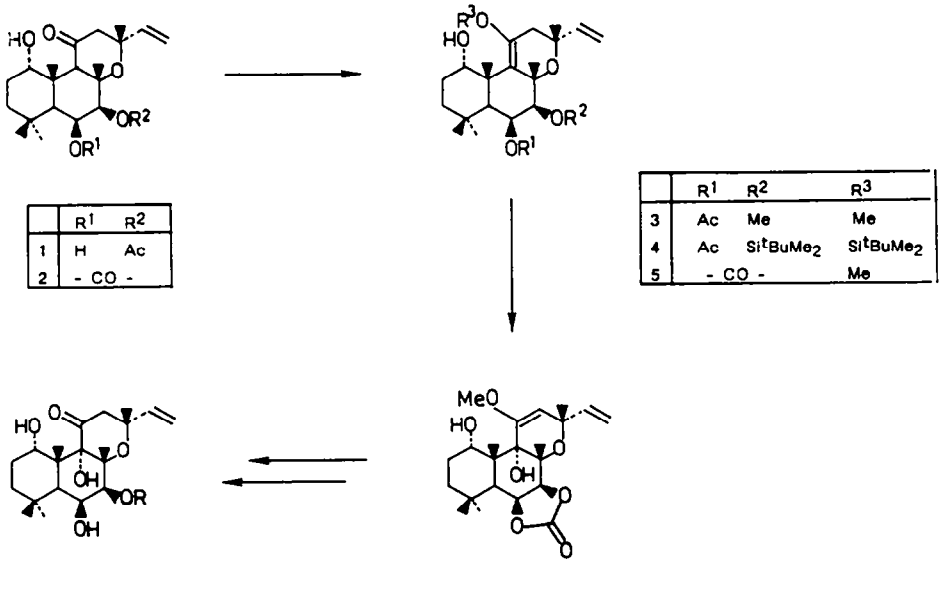
Abstract - According to trapping experiments the 1,9-dideoxyforskolin derivatives **10** and **12** react with KH in THF exclusively to form the corresponding 9(11)-enolates. Reaction of enol ethers **14** and **16** with m-chloroperbenzoic acid leads to the 12α-silyloxy ketones **20** and **21**, respectively.

From the Indian medicinal herb Coleus forskohlii Briq. (Labiatae) a number of novel 11-oxomannoyl oxide derivatives including forskolin (**6**),[1] 9-deoxyforskolin (**1**),[2] and 1,9-dideoxyforskolin (**9**)[1] have been isolated. Whereas forskolin (**6**) is a unique adenylate cyclase activator and has been shown to exhibit strongly inotropic, antihypertensive, and bronchospasmolytic activities, **1** and **9** lack these interesting physiological properties.[3] Since the plant material is currently the sole source of **6**[4] finding a method for the conversion of **1** and **9** to **6** would be very useful. The oxidation sequence **9** → **19** → **6** is also of interest in conjunction with a potential synthetic route from farnesol to **6**.[5]



	R^1	R^2
1	H	Ac
2	- CO -	

	R^1	R^2	R^3
3	Ac	Me	Me
4	Ac	Si^tBuMe_2	Si^tBuMe_2
5	- CO -		Me

	R
6	Ac
7	H

Scheme 1.

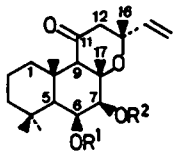
Two recent publications addressed this problem:

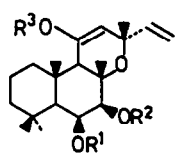
a) Microbial oxidation of deacetyl-1,9-dideoxyforskolin (**13**) was reported to produce **7** by introduction of both the 1α- and the 9α-OH group, but the yield was very low (0.76%).[6]

b) As reported by Hrib,[7] 9-deoxyforskolin (**1**) reacts with KH in THF solution to form the 9(11)-enolate which can be trapped with either tert-butyldimethylsilyl chloride or dimethyl sulfate to give the 9(11)-enol derivatives **3** and **4**, respectively. These reactions are accompanied by acetyl group migration. Similarly, the cyclic carbonate **2** was converted into the methyl enol ether **5** in 62% yield. Whereas the enolic double bond of the silyl ether **4** resisted oxidation with m-chloroperbenzoic acid (MCPBA), the oxidation of **5** proceeded regio- and stereoselectively to provide the oxidation product **8**, from which forskolin (**6**) was obtained in 12% overall yield.[7]

In principle, the exclusive formation of the 9(11)-enolate from **1** appears somewhat surprising. We have recently studied the enol ether formation from 1,9-dideoxyforskolin (**9**) under various conditions, and we have been unable to detect even a trace of the 9(11)-isomer.[5] We describe herein experiments which demonstrate that 1,9-dideoxyforskolin (**9**) gives completely different results from those reported for **1** when submitted to Hrib's reaction conditions.[7]

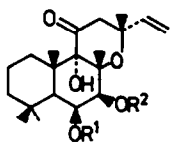
In order to suppress the undesired acetyl migration, the known trimethylsilyl ethers **10** and **12**[5] were chosen as starting materials. Treatment of **10** with KH in THF and then reacting the intermediate enolate with tert-butyldimethylsilyl chloride gave enol ether **14** (62%) along with 17% of the hydrolysis product **18** which was formed under the work-up conditions. Trapping the enolate with dimethyl sulfate afforded a 73% yield of enol ether **15**. The ^{1}H NMR spectra of these compounds revealed immediately the enolic double bond to be in the 11(12)-position in contrast to the cases reported by Hrib.[7] Fig. 1 shows part of the 80 MHz ^{1}H NMR spec-

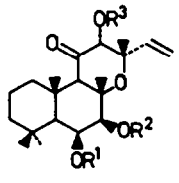




	R^1	R^2
9	H	Ac
10	$SiMe_3$	Ac
11	Ac	H
12	Ac	$SiMe_3$
13	H	H

	R^1	R^2	R^3
14	$SiMe_3$	Ac	Si^tBuMe_2
15	$SiMe_3$	Ac	Me
16	Ac	$SiMe_3$	Si^tBuMe_2
17	Ac	$SiMe_3$	Me
18	$SiMe_3$	H	Si^tBuMe_2





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	R^1	R^2	R^3
20	$SiMe_3$	Ac	Si^tBuMe_2
21	Ac	$SiMe_3$	Si^tBuMe_2

Scheme 2.

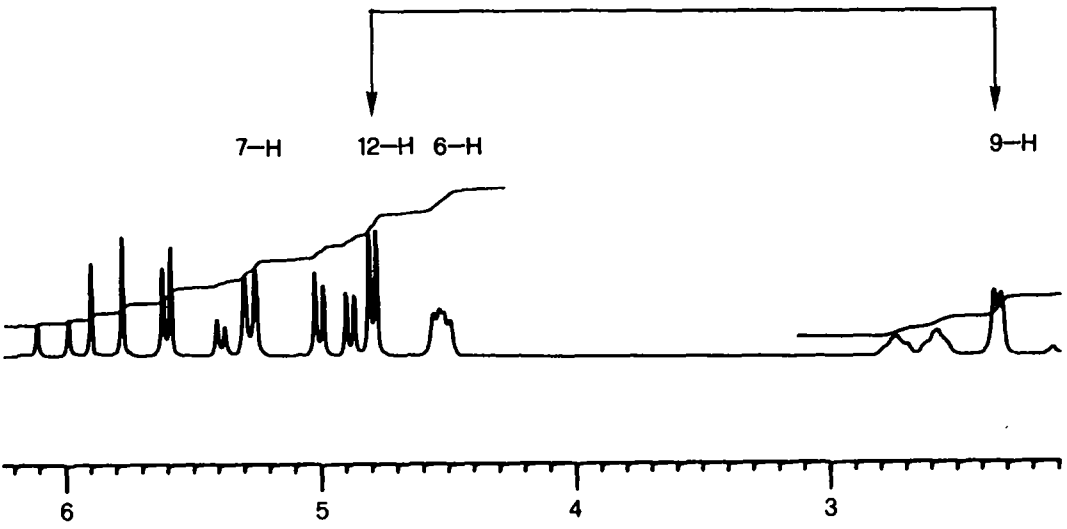
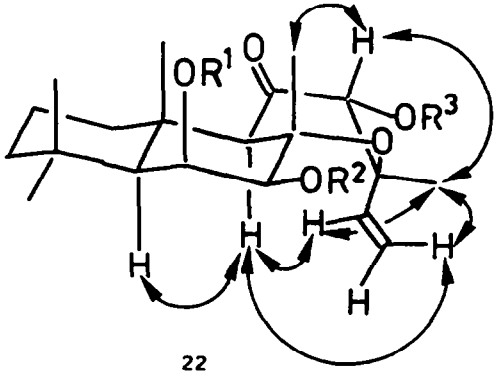


Fig. 1. 80 MHz ^{1}H NMR spectrum of **14** in C_6D_6 (δ = 2.1-6.2 region).

trum of **14**. The 9α-H and 12-H signals are clearly visible as well as the long-range coupling between these two protons. In the same way **12** was converted into **16** (86%) and **17** (94%), respectively. Oxidation of **16** with MCPBA in CH_2Cl_2 solution containing K_2CO_3 proceeded as expected[8] and resulted in the isolation of α-silyloxy ketone **21** in 43% yield. 40% of **16** were recovered. Reaction of **14** with MCPBA produced α-silyloxy ketone **20** in 31% yield and a second major oxidation product the structure of which was not elucidated. In contrast to the rather clean oxidation reactions of **14** and **16**, the corresponding methyl enol ethers **15** and **17** upon oxidation with MCPBA yielded complicated mixtures of oxidation products which were not further investigated. The configuration of the newly introduced 12-silyloxy group in both **20** and **21** was evident from NOE difference experiments which revealed the existence of a nuclear Overhauser enhancement between 12-H and CH_3-17 (see formula **22**). The NOE enhancements indicated in formula **22** are best accomodated assuming a boat or twist conformation of ring C and a rotating vinyl group (around the C-13 - C-14 bond).

In conclusion, formation of the 9(11)-enolate and the corresponding enol ethers, respectively, from 1,9-dideoxyforskolin is obviously a rather unlikely process. Compounds of type **19** seem not accessible via this route. Speculations on how the 1α-OH group influences the reactivity of **1** so strikingly[7] seem premature without further experimental work.



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EXPERIMENTAL

General

All reactions were performed in oven-dried glassware under a positive pressure of argon. Liquids and solutions were transferred by syringe, and were introduced into the reaction flasks through rubber septa. If not otherwise stated reactions were performed in Wheaton serum bottles sealed with aluminium cap with open top and Teflon-faced septum (Aldrich). The potassium hydride used in this work was obtained from a 20-25% mineral oil suspension by briefly stirring it in an argon atmosphere with THF (three times), allowing the hydride to settle, removing the solvent with a syringe, and finally drying in vacuo over P_2O_5. Dimethyl sulfate was used freshly distilled from calcium hydride. The instrumentation used was: ^{1}H NMR: WP 80 (Bruker), AM 400 (Bruker); ^{13}C NMR: AM 400 (Bruker); IR: Perkin Elmer 257 and 681; MS: MAT-731 and MAT-CH-5 (Varian); LC: Medium pressure chromatography (MPLC) using 31.0 cm x 2.5 cm (column B, 60g SiO_2) and 37.0 cm x 1.5 cm (column A, 17 g SiO_2) glass tubes, silica gel 50 µm, (Grace), Duramat pump (CfG); UV detector Chromatochord III (Serva).

14 and 18 from 10.

A solution of **10** (45.9 mg, 0.102 mmol) in THF (0.5 ml) was added at 20°C to a solution of ^{t}BuMe$_2$SiCl (46.1 mg, 0.306 mmol) in THF (0.5 ml) containing suspended KH (36.8 mg, 0.918 mmol). The reaction mixture was stirred at 20°C for 3 h. After destroying the excess KH by addition of tert-butyl alcohol (77 µl, 0.816 mmol) at 0°C, the mixture was directly filtered through SiO_2 (3g) covered with Florisil (2g), elution with hexanes-ethyl acetate-NEt_3 50:1:0.05. Chromatographic purification (a: 7g SiO_2 (hexanes-ethyl acetate 60:1), b: 5g SiO_2 (hexanes-ethyl acetate 100:1) gave **10** (3.1 mg, 7%), 14 (35.3 mg, 62%), and **18** (9.1 mg, 17%). According to TLC control both **10** and **18** were formed during the working-up procedure.

7β-Acetoxy-8,13-epoxy-6β-trimethylsilanyloxy-11-(tert-butyl-dimethylsilanyloxy)-labd-11,14-diene (14).

M.p. 113-115°C (from EtOH).- ^{1}H NMR (80 MHz, C_6D_6): δ = 0.20 (s, 15H, $Si(CH_3)_2$ + $Si(CH_3)_3$), 0.86 (s, 3H, CH_3), 0.98 (s, 9H, $C(CH_3)_3$), 1.20 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.89 (s, 3H, OAc), 2.32 (d, 1H, 9-H), 2.47-2.84 (m, 1H), 4.52 (dd, 1H, 6-H), 4.79 (d, 1H, 12-H), 4.93 (dd, 1H, 15-H), 5.28 (d, 1H, 7-H), 5.50 (dd, 1H, 15'-H), 6.93 (dd, 1H, 14-H). $J_{9,12}$=2.0Hz, $J_{6,5}$=2.0Hz, $J_{6,7}$=3.5Hz, $|J_{15,15'}|$=2.5Hz, $J_{15,14}$=10.0Hz, $J_{15',14}$=17.0Hz.- IR (CCl_4): 1740 (CO), 1645 cm^{-1} (C=C).- MS: m/z (%) = 549 (17, $(M-CH_3)^+$), 225 (60), 73 (100).- (Found C, 66.04; H, 9.95. $C_{31}H_{56}O_5Si_2$ (564.9) requires C, 65.91; H, 9.99%).

8,13-Epoxy-7β-hydroxy-6β-trimethylsilanyloxy-11-(tert-butyl-dimethylsilanyloxy)-labd-11,14-diene (18).

^{1}H NMR (80 MHz, C_6D_6): δ = 0.22-0.38 (s, 15H, $SiCH_3$ signals), 0.96 (s, 3H , CH_3), 1.00 (s, 9H, $C(CH_3)_3$), 1.30 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 2.14 (d, 1H, 7-OH), 2.37 (d, 1H, 9-H), 2.50-2.87 (m, 1H), 3.52 (dd, 1H, 7-H), 4.52 (dd, 1H, 6-H), 4.74 (d, 1H, 12-H), 4.90 (dd, 1H, 15-H), 5.25 (dd, 1H, 15'-H), 5.91 (dd, 1H, 14-H). $J_{7,OH}$=3.0Hz, $J_{9,12}$=2.5Hz, $J_{7,6}$=2.0Hz, $J_{6,5}$=3.5Hz, $|J_{15,15'}|$=2.0Hz, $J_{15,14}$=10.0Hz, $J_{15',14}$=17.0Hz.- IR (CCl_4): 3590 (OH), 1740 und 1645 cm^{-1} (C=C).- MS: m/z (%) = 507 (19, $(C_{29}H_{54}O_4Si_2-CH_3)^+$), 225 (34), 73 (100).

Oxidation of 14 with MCPBA.

To a solution of **14** (88.4 mg, 0.157 mmol) in CH_2Cl_2 (1 ml), containing K_2CO_3 (108.4 mg, 0.784 mmol) was slowly added at -78°C a solution of MCPBA (135.3 mg, 0.627 mmol). After being allowed to warm

slowly to 0°C, the mixture was stirred at 0°C for 24 h. Then again MCPBA (67.7 mg, 0.314 mmol) was added and the mixture stirred at 0°C for another 26 h. Filtration through SiO_2 (8 g) covered with Florisil (2 g) (elution with hexanes-ethyl acetate 50:1), solvent evaporation, and MPLC (column A, hexanes-acetone 80:1) gave **20** (28.2 mg, 31%), **14** (8.1 mg, 9%) and 22.7 mg of a more polar compound of unknown structure.

7β-Acetoxy-8,13-epoxy-6β-trimethylsilanyloxy-12α-(tert-butyl-dimethylsilanyloxy)-labd-14-en-11-one (20).

^{1}H NMR (400 MHz, C_6D_6): δ = 0.13-0.36 (s, 15H, $SiCH_3$ signals), 0.72 (s, 3H, CH_3-18), 1.00 (s, 9H, $C(CH_3)_3$), 1.12 (s, 3H, CH_3-20), 1.42 (s, 3H, CH_3-16), 1.60 (s, 3H, CH_3-19), 1.69 (s, 3H, CH_3-17), 1.98 (s, 3H, OAc), 2.82 (m, 1H), 3.26 (s, 1H, 9-H), 4.07 (s, 1H, 12-H), 4.43 (dd, 1H, 6-H), 5.20 (dd, 1H, 15-H), 5.44 (d, 1H, 7-H), 6.00 (dd, 1H, 15'-H), 6.30 (dd, 1H, 14-H). $J_{6,7}$=3.5Hz, $J_{6,5}$= 2.0Hz, $|J_{15,15'}|$=2.0Hz, $J_{15,14}$=11.0Hz, $J_{15',14}$=17.5Hz.- ^{13}C-NMR (100.6 MHz, DEPT, C_6D_6)[9]: δ = -5.24 ($Si(CH_3)$), -3.59 ($Si(CH_3)$), 0.78 ($Si(CH_3)_3$), 17.27 (C-20), 18.71 (C-2), 21.13 (C-17), 23.48 ($OCOCH_3$), 25.78 (C-19), 26.15 ($C(CH_3)_3$), 30.47 (C-16), 32.83 (C-18), 34.04 (C-4), 38.68 (C-10), 41.98 (C-1), 43.93 (C-3), 55.70 (C-5), 64.69 (C-7), 71.84 (C-9), 77.46 and 78.91 (C-8 and C-13), 79.92 (C-6), 81.33 (C-12), 115.45 (C-15), 142.16 (C-14), 169.66 ($OCOCH_3$), 205.97 (C-11).- IR (CCl_4): 1735 cm^{-1} (CO).- MS: m/z (%) = 510 (10), 453 (10), 393 (18), 363 (10), 319 (25), 303 (23), 229 (33), 225 (100), 73 (82).- (Found C, 64.20; H, 9.68. $C_{31}H_{56}O_6Si_2$ (580.9) requires C, 64.09; H, 9.72).

6β-Acetoxy-8,13-epoxy-7β-trimethylsilanyloxy-11-(tert-butyl-dimethylsilanyloxy)-labd-11,14-diene (16).

16 was prepared from **12** exactly as described for **14** (filtration through SiO_2 (3 g) covered with Florisil (2 g) with hexanes-ethyl acetate-NEt_3 50:1:0.05). Yield: 86%.- M.p. 151-154°C (from EtOH). - ^{1}H NMR (80 MHz, C_6D_6): δ = 0.30-0.50 (s, 15H, $SiCH_3$ signals), 1.11 (s, 12H, $C(CH_3)_3$ + CH_3), 1.13 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.92 (s, 3H, OAc), 2.30 (d, 1H, 9-H), 2.65-3.00 (m, 1H), 3.85 (d, 1H, 7-H), 4.90 (d, 1H, 12-H), 5.02 (dd, 1H, 15-H), 5.40 (dd, 1H, 15'-H), 5.93 (m, 1H, 6-H), 6.06 (dd, 1H, 14-H). $J_{9,12}$=2.0Hz, $J_{7,6}$=6.0Hz, $J_{15,14}$=10.0Hz, $|J_{15,15'}|$=2.0Hz, $J_{15',14}$=18.0Hz.- IR (CCl_4): 1745 (CO), 1650 cm^{-1} (C=C).- MS: m/z (%) = 549 (14, $(M-CH_3)^+$), 459 (18), 73 (100).- (Found C, 65.88; H, 10.00. $C_{31}H_{56}O_5Si_2$ (564.9) requires C, 65.91; H, 9.99).

6β-Acetoxy-8,13-epoxy-7β-trimethylsilanyloxy-12α-(tert-butyl-dimethylsilanyloxy)-labd-14-en-11-one (21).

21 was prepared from **16** exactly as described for **20**. MPLC (hexanes-ethyl acetate 150:1) gave **21** (15.7 mg, 43%) and **16** (14.5 mg, 40%).- M.p. 106-109°C (from EtOH).- ^{1}H NMR (400 MHz, C_6D_6): δ = 0.12-0.33 (s, 15H, $SiCH_3$ signals), 0.92 (s, 3H, CH_3-20), 0.96 (s, 3H, CH_3-19), 1.01 (s, 9H, $C(CH_3)_3$), 1.42 (s, 3H, CH_3-16), 1.55 (s, 3H, CH_3-18), 1.64 (s, 3H, CH_3-17), 1.75 (s, 3H, OAc), 2.82 (m, 1H), 3.10 (s, 1H, 9-H), 3.94 (d, 1H, 7-H), 4.09 (s, 1H, 12-H), 5.10 (dd, 1H, 15-H), 5.53 (dd, 1H, 15'-H), 5.80 (dd, 1H, 6-H), 6.29 (dd, 1H, 14-H). $J_{7,6}$=4.5Hz, $|J_{15,15'}|$=2.0Hz, $J_{15,14}$=10.5Hz, $J_{15',14}$=17.5Hz, $J_{6,5}$=2.2Hz.- ^{13}C NMR (100.6 MHz, C_6D_6)[9]: δ = 0.43 ($Si(CH_3)_3$), 16.99 (C-20), 18.65 (C-2 + $C(CH_3)_3$), 20.98 (C-17), 23.15 ($OCOCH_3$), 24.52 (C-19), 26.13 ($C(CH_3)_3$), 29.08 (C-16), 32.92 (C-18), 33.99 (C-4), 38.35 (C-10), 41.59 (C-1), 44.11 (C-3), 54.52 (C-5), 64.21 (C-7), 71.92 (C-9), 79.07 and 79.21 (C-8 and C-13), 80.33 (C-6 + C-12), 114.19 (C-15), 143.09 (C-14), 169.41 ($OCOCH_3$), 206.40 (C-11).- IR (CCl_4): 1745 und 1730 cm^{-1} (CO).- MS: m/z (%) = 565 (1, $(M-CH_3)^+$), 510 (23), 453 (74), 393 (65), 117 (47), 73 (100).- (Found C, 64.29; H, 9.80. $C_{31}H_{56}O_6Si_2$ (580.9) requires C, 64.09 H, 9.72).

7β-Acetoxy-8,13-epoxy-11-methoxy-6β-trimethylsilanyloxy-labd-11,14-diene (15).

A solution of **10** (51.3 mg, 0.114 mmol) in THF (0.5 ml) was added to a solution of Me_2SO_4 (32.3 µl, 0.342 mmol) in THF (0.5 ml) containing KH (41.2 mg, 1.026 mmol). The reaction mixture was stirred at 20°C for 7h. After the excess KH was destroyed by addition of tert-butyl alcohol (86 µl, 0.912 mmol) at 0°C (reaction time: 5 min), the mixture was filtered through SiO_2 (5g) covered with Florisil (3g) (elution with hexanes-ethyl acetate-NEt_3 50:1:0.05). MPLC (column A, hexanes-ethyl acetate 60:1) gave **15** (37.7 mg, 73%).- M.p. 101-103°C (from EtOH).- ^{1}H NMR (80 MHz, C_6D_6): δ = 0.21 (s, 9H, $Si(CH_3)_3$), 0.85 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.90 (s, 3H, OAc), 2.36 (d, 1H, 9-H), 2.44-2.79 (m, 1H), 3.10 (s, 3H, OCH_3), 4.36 (d, 1H, 12-H), 4.53 (dd, 1H, 6-H), 4.94 (dd, 1H, 15-H), 5.29 (d, 1H, 7-H), 5.48 (dd, 1H, 15'-H), 5.91 (dd, 1H, 14-H). $J_{9,12}$=2.0Hz, $J_{6,7}$=3.5Hz, $J_{6,5}$=2.0Hz, $|J_{15,15'}|$=2.5Hz, $J_{15,14}$=10.0Hz, $J_{15',14}$= 17.0Hz.- IR (CCl_4): 1740 (CO), 1650 cm^{-1} (C=C).- MS: m/z (%) = 449 (36, $(M-CH_3)^+$), 225 (90), 73 (65), 43 (100).- (Found C, 67.23; H, 9.52. $C_{26}H_{44}O_5Si$ (464.7) requires C, 67.20; H, 9.54).

6β-Acetoxy-8,13-epoxy-11-methoxy-7β-trimethylsilanyl-labd-11,14-diene (17).

17 was prepared from **12** as described for **15**. Pure **17** (94%) was obtained without chromatographic separation.- M.p. 120-124°C (from EtOH).- ^{1}H NMR (80 MHz, C_6D_6): δ = 0.36 (s, 9H, $Si(CH_3)_3$), 1.00 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 1.80 (s, 3H, OAc), 2.21 (d, 1H, 9-H), 2.51-2.86 (m, 1H), 3.10 (s, 3H, OCH_3), 3.75 (d, 1H, 7-H), 4.36 (d, 1H, 12-H), 4.91 (dd, 1H, 15-H), 5.29 (dd, 1H, 15'-H), 5.82 (dd, 1H, 6-H), 5.94 (dd, 1H, 14-H). $J_{9,12}$=2.2Hz, $J_{7,6}$=4.5Hz, $|J_{15,15'}|$=2.5Hz, $J_{15,14}$=10.0Hz, $J_{15',14}$=17.0, $J_{6,5}$=2.0Hz.- IR (CCl_4): 1745 (CO), 1650 cm^{-1} (C=C).- MS: m/z (%) = 449 (45, $(M-CH_3)^+$), 359 (42), 299 (22), 117 (34), 73 (94), 43 (100).- (Found C, 67.30; H, 9.58. $C_{26}H_{44}O_5Si$ (464.7) requires C, 67.20; H, 9.54).

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