CROATICA CHEMICA ACTA CCACAA 58 (4) 491—509 (1985)

CCA-1599

YU ISSN 0011-1643
UDC 547.914
Original Scientific Paper

Structure-Activity Relationships in Odor Perception of Drimane Derivatives*

*Günther Ohloff*** *and Wolfgang Giersch*

Firmenich SA, Research Laboratories, CH-1211, Geneva 8

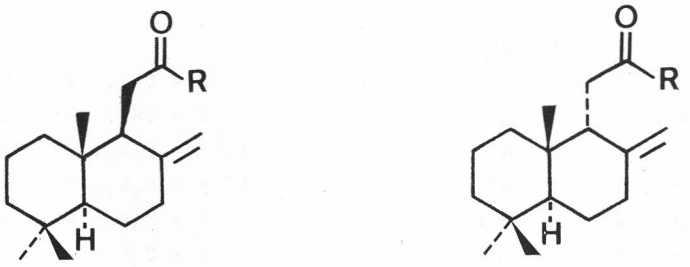
Received April 4, 1985

The woody, ambergris-like odor of *trans*-decalone derivatives of type **5** increases with the introduction of equatorial alkyl substituents in the C(9)-position and decreases drastically in the corresponding 9-epi derivatives. Complete stereocontrol of odor perception has been observed for the diastereoisomers of γ-bicyclohomofarnesal **1** and **2**. A similar tendency in odor perception has been recognized in substituted alcohols of type **12**. The sandalwood-like ambergris note found in Polywood(R) (**14**) disappeared in corresponding alkyl substituted acetates. The molecular basis of the 'steroid-type' scent of some esters of type **39** was hitherto unknown.

INTRODUCTION

(—)-γ-Bicyclohomofarnesal (**1**) and the corresponding methyl ketone (**3**)[1], oxidative degradation products of (—)-sclareol[2], are ambergris odorants of the finest quality[1]. Surprisingly, in the poor odor profile of the diastereoisomers **2** and **4**, this particular tonality is lacking, although the 'triaxial rule' of odor sensation[1] seems to be fulfilled in all cases. While searching for an explanation for this phenomenon systematic experiments of stereochemistry and odor

Scheme 1

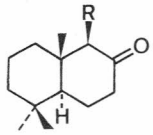


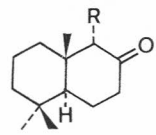
1 R = H **2**

3 R = CH_3 **4**

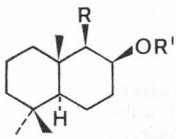
* Dedicated to Prof. Dr. M. Lj. Mihailović on the occasion of his 60th birthday.
** To whom correspondence should be addressed.

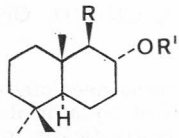
Scheme 2

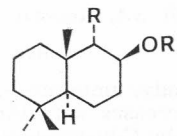


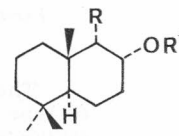


5 R = H
6 R = CH_3 **7**
8 R = C_2H_5 **9**
10 R = C_3H_7 **11**

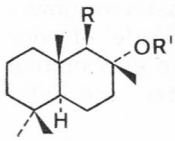


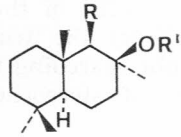


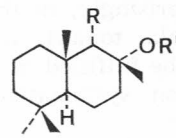


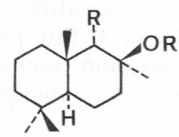


12 R = R' = H **13**
14 R = H; R' = Ac **15**
16 R = CH_3; R' = H **17**
18 R = CH_3; R' = H **19**
20 R = CH_3; R' = Ac
21 R = CH_3; R' = Ac
22 R = C_2H_5; R' = H **23**
24 R = C_2H_5; R' = H
25 R = C_2H_5; R' = Ac **26**
27 R = C_2H_5; R' = Ac
28 R = C_3H_7; R' = H **29**
30 R = C_3H_7; R' = H
31 R = C_3H_7; R' = Ac **32**
33 R = C_3H_7; R' = Ac









34 R = R' = H
35 R = H; R' = Ac **36**
R = CH_3; R' = H **37**
R = CH_3; R' = H **38**
R = CH_3; R' = Ac **39**
R = CH_3; R' = Ac **40**
41 R = C_2H_5; R' = H **42**
43 R = C_2H_5; R' = H **44**
45 R = C_2H_5; R' = Ac **46**
47 R = C_2H_5; R' = Ac **48**
49 R = C_3H_7; R' = H **50**
R = C_3H_7; R' = H **51**
52 R = C_3H_7; R' = Ac **53**
R = C_3H_7; R' = Ac **54**

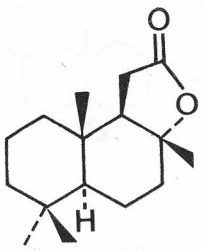
were carried out on derivatives in the drimane and labdane series, whose structure modifications only concern C(8) and C(9). Our main interest concerned the introduction of diastereoisomeric alkyl substituents with varying chain lengths on C(9) of well known ambergris-type molecules. The bicyclic ketone **5**[1] served as model, together with ester **14** (Polywood®), and its odorless diastereoisomer **15**[3].

The odor of ketone **5** intensifies in the methyl- and ethyl-substituted derivatives of the equatorial series **6** and **8**. The same tonality predominates in the propyl derivative **10** but with diminution of odor intensity. In the axial series **7**, **9**, **11** odor strength diminishes already in the first member **7**. Ketone **9** possesses little odor and **11** is practically odorless. The odors of the secondary alcohols were highly dependent on polarity and stereochemistry. The strongest amber note is found in the 9-ethyl derivative **22**; it is much less in higher and lower homologs **16** and **28** and disappears completely in the unsubstituted alcohol **12**[4]. The 8-epihomologs **13**, **17**, **23** and **29** are odorless as are the 9-epi derivatives **18**, **19**, **24** and **30**. Among the tertiary alcohols 9-nordrimanol **34** possesses an outstanding amber-like odor[5], diminishing in the homologs **41** and **49**. The 9-epi derivative **43** has a faint animal odor or like cold cigar ash without any amber note, whereas its diastereoisomers **38**, **44** and **51** are odorless. The corresponding esters had a different odor from the alcohols. Whereas Polywood® (**14**) is known to have a distinct odor character, the introduction of an equatorial methyl group leads to an important diminution of the sandalwood-like amber note in ester **20**, an odor which disappears completely in the higher homologs **25** and **31**. All 8α-acetates **15**, **26** and **32** were odorless. Similar observations were made in the 9-epi series. The Polywood character appears diminished in acetate **21**, whereas the other esters **27** and **33** are almost odorless. An extremely faint odor is found in the known esters **35** and **36**[1] and also in the homologs **45** and **52**. Surprisingly, acetate **46** possesses a strong urine- and perspiration-like note, mostly found in certain steroids[6] and their related seco-compounds[7]. This steroid-type scent is also found in the lower and higher homologs **39** and **53**, although here it is diminished and has a woody undertone. An explanation of the molecular basis for this phenomenon is not yet possible. Of the 9-epi compounds, only **47** exhibited a faint amber note, while the acetates **40**, **48** and **54** were odorless.

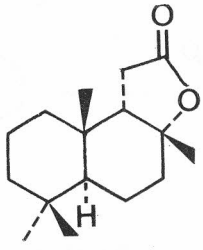
SYNTHESES

The common precursors for all compounds described in this work are the diastereoisomeric lactones (+)-sclareolide (**I**)[8] and 9-epi-sclareolide (**XV**)[9], derived from the labdane diterpenediol (—)-sclareol.

Scheme 3



I



XV

Transformations of both lactones **I** and **XV** into the target molecules have been achieved by literature procedures and are described in abbreviation in the experimental part.

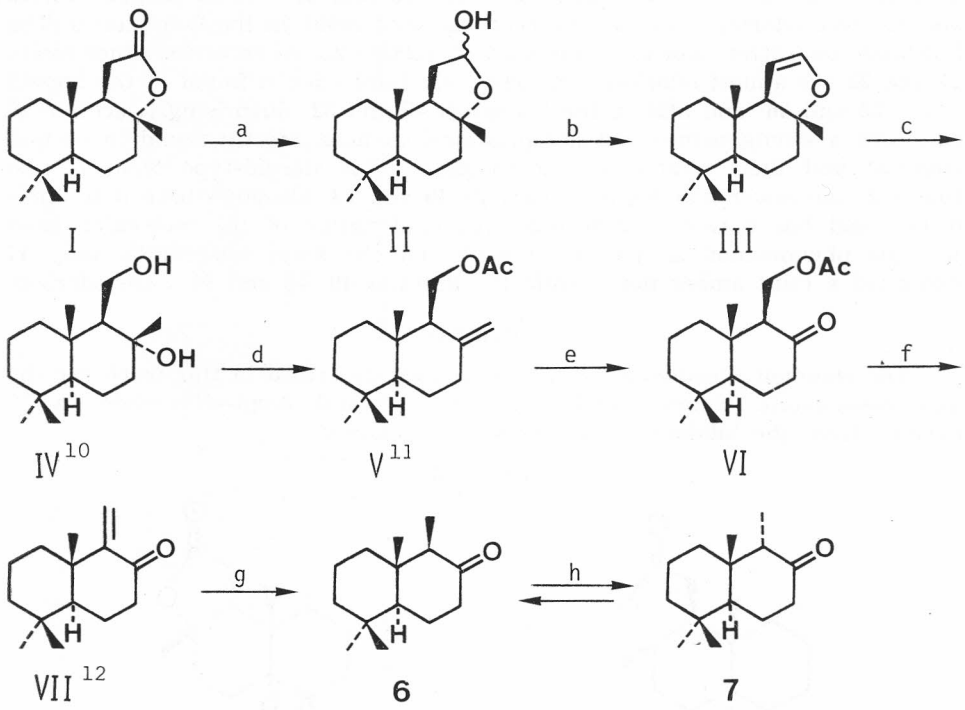
EXPERIMENTAL

(with the valuable collaboration of *Eliane Cristoforetti* and *Beatrice Frei*)

Melting points (m. p.) are not corrected. Specific rotations ($[\alpha]_D$) were measured in $CHCl_3$ at 20° as ~ 1% solution with a Perkin Elmer 141 polarimeter. Preparative column chromatography was performed on silicagel (Merck 60, less than 230 mesh). Gas chromatography (GC) was carried out on a) Carlo Erba Fractovap 4200 using glass columns (ID = 3 mm) 3 m Carbowax (15%) or 3 m SE 30 (15%) on Chromosorb W, 60—90 mesh; b) Carlo Erba Fractovap 2900 using capillary columns (Chrompack): 1. 10 m and Bruker HX 90; measurements were run in $CDCl_3$ with tetramethylsilane as spectra was carried out on the following apparatus. IR: Perkin-Elmer 297; characteristic band positions are given in cm^{-1}. ^1H- and ^{13}C-NMR:Bruker WH 360 and Bruker HX 90; measurements were run in $CDCl_3$ with tetramethylsilane as internal standard ($\delta = 0.00$ ppm); abbreviations: *s*, singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *br* = broad, *J* = spin-spin coupling constant in Hz, $w_{1/2}$ = half-width in Hz. MS: Varian MAT 112, using electrons of ca. 70 eV energy. — The starting material for all products was sclareolide (**I**)* (m. p. 123—125°; $[\alpha]_D^{20} = +43°$) from Reynolds, USA. Numbering and configurations follow Chem. Abstr. nomenclature.

Preparation of Compounds **6** *and* **7**.

Scheme 4



Reagents: a) Al(*i*-Bu)$_2$H, toluene/-78°[13]; b) (Ac)$_2$O, pyridine, then pyrolyzed in N_2-stream at 350°; c) O_3/EtOH/-70°, then $NaBH_4 \rightarrow$ RT.; d) (Ac)$_2$O, pyridine/reflux/20 h; e) O_3/AcOEt/-70°, then reduced with Zn-powder/acetic acid; f) N_2-stream/470°; g) PtO_2/AcOEt, H_2; h) NaOMe, MeOH/reflux/1 h; after 1 h equilibrium was reached. already reached.

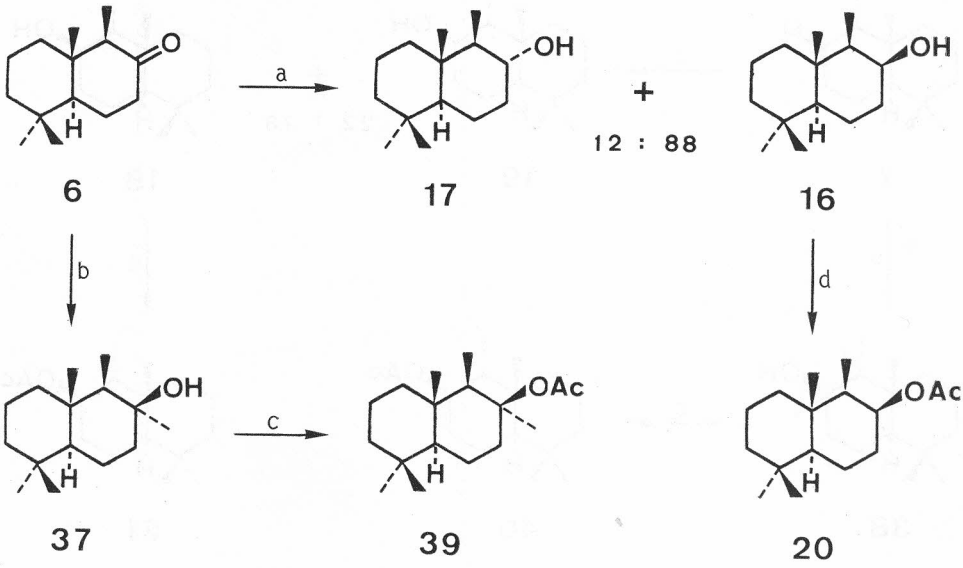
* Roman numerals are used throughout this work for starting materials and intermediates not submitted to sensory evaluation.

12-Nordriman-8-one (**6**). The product was crystallized from pentane: m.p. 58—60°, $[\alpha]_D^{20} = -83°$. IR: 1720. ^{1}H-NMR: 0.73 (*s*, 3H, 0.88 (*s*, 3H), 0.90 (*d*, $J = 6$, 3H), 0.99 (*s*, 3H). MS: 208 (58, $M^{+\cdot}$), 193 (13), 175 (22), 166 (26), 137 (76), 123 (69), 109 (43), 95 (78), 81 (85), 67 (66), 55 (80), 41 (100).

(9βH)-12-Nordriman-8-one (**7**). The product was purified by chromatography on SiO_2 (Merck 60) at 4 bars with cyclohexane/ether 98 : 2. $[\alpha]_D^{20} = -28.5°$. ^{1}H-NMR: 0.874 (*s*, 3H), 0.936 (*s*, 3H), 0.975 (*s*, 3H), 1.105 (*d*, $J = 7$, 3H). MS: 208 (33, $M^{+\cdot}$), 193 (8), 175 (24), 166 (28), 137 (53), 123 (53), 109 (39), 95 (60), 81 (67), 55 (71), 41 (100).

Preparation of Compounds **16**, **17**, **20**, **37** *and* **39**.

Scheme 5



Reagents: a) $LiAlH_4$, THF/reflux/2 h; b) MeLi, ether; after 48 h reflux only 60% transformation; c) $(Ac)_2O$, CH_3COCl/pyridine/40°/4 h[14]; d) $(Ac)_2O$, pyridine/100°/1 h.

16 and **17** were purified by chromatography on SiO_2 with cyclohexane/ether 95 : 5.

12-Nordriman-8β-ol (**16**). M.p. 65—66°, $[\alpha]_D^{20} = 0°$. IR ($CDCl_3$): 3650, 3480. ^{1}H-NMR: 0.86 (*s*, 3H), 0.88 (*s*, 3H), 0.99 (*s*, 3H), 0.945 (*d*, $J = 7$, 3H), 3.76 (*m*, $w_{1/2} = 6$, 1H). MS: 210 (6, $M^{+\cdot}$), 192 (13), 177 (51), 137 (36), 124 (83), 109 (87), 95 (62), 81 (72), 69 (67), 55 (75), 41 (100).

12-Nordriman-8α-ol (**17**). M.p. 78—80°, $[\alpha]_D^{20} = -35.4°$. ^{1}H-NMR: 0.783 (*s*, 3H), 0.816 (*s*, 3H), 0.875 (*s*, 3H), 0.91 (*d*, $J = 6$, 3H), 3.37 (*ddd*, $J_1 = 5$, $J_2 = J_3 = 10$, 1H). MS: 210 (2, $M^{+\cdot}$), 192 (23), 177 (66), 163 (28), 137 (82), 124 (54), 109 (78), 95 (64), 81 (72), 69 (68), 55 (78), 41 (100).

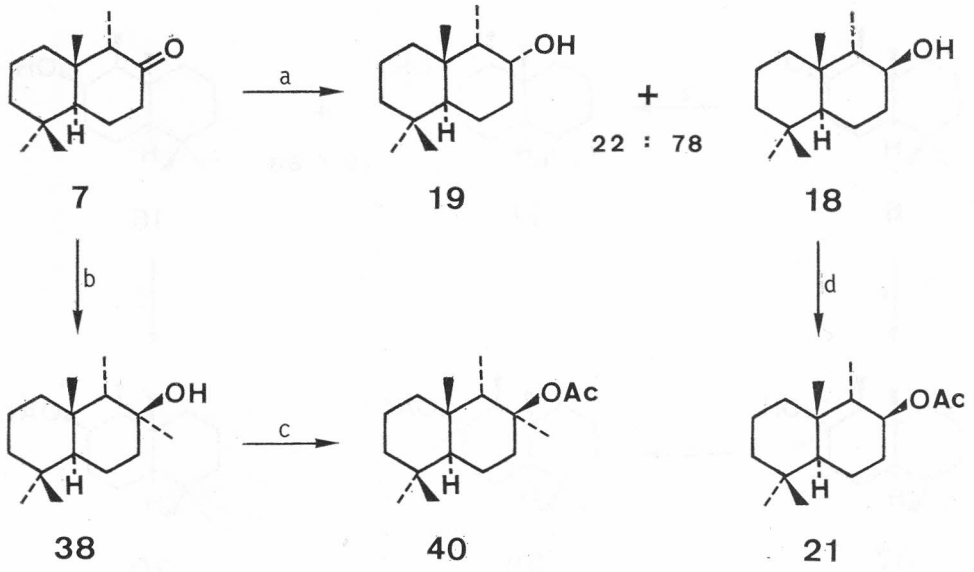
12-Nordriman-8β-yl Acetate (**20**). $[\alpha]_D^{20} = +32.4°$. IR: 1740. ^{1}H-NMR: 2.1 (*s*, 3H), 4.9 (*m*, 1H). MS: 252 (0, $M^{+\cdot}$), 192 (22), 177 (46), 149 (27), 136 (36), 124 (72), 109 (43), 95 (42), 81 (51), 69 (42), 55 (42), 43 (100).

Driman-8β-ol (**37**). $[\alpha]_D^{20} = -12.3°$. IR ($CDCl_3$): 3630, 3470. ^{1}H-NMR: 0.845 (*s*, 3H), 0.873 (*s*, 3H), 0.895 (*d*, $J = 7$, 3H), 0.947 (*s*, 3H), 1.12 (*s*, 3H). MS: 224 (7, $M^{\cdot+}$), 209 (13), 191 (53), 177 (21), 153 (17), 137 (23), 123 (24), 109 (63), 97 (53), 83 (60), 71 (91), 55 (67), 43 (100).

Driman-8β-ul Acetate (**39**). $[\alpha]_D^{20} = +36.6°$. IR: 1740. ^{1}H-NMR: 0.88 (*s*, 3H), 0.90 (*d*, $J \approx 5$, 3H), 0.95 (*s*, 3H), 1.47 (*s*, 3H), 2.0 (*s*, 3H). MS: 266 (0, $M^{\cdot+}$), 206 (34), 191 (41), 136 (24), 124 (56), 109 (93), 95 (40), 82 (96), 69 (40), 55 (37), 43 (100).

Preparation of Compounds **18**, **19**, **21**, **38** *and* **40**.

Scheme 6



Reagents: a) $LiAlH_4$, THF/reflux/2 h; b) MeLi, ether; after 7 days reflux only 50% transformation; c) $(Ac)_2O$, CH_3COCl/pyridine/40°/8 h[14]; d) $(Ac)_2O$, pyridine/100°/1 h.

18 and **19** were purified by chromatography on SiO_2 with cyclohexane/ether 95 : 5.

(9βH)-12-Nordriman-8β-ol (**18**). $[\alpha]_D^{20} = -39.7°$. ^{1}H-NMR: 0.845 (*s*, 3H), 0.873 (*s*, 3H), 0.905 (*d*, $J = 7$, 3H), 1.24 (*s*, 3H), 3.82 (*m*, $w_{1/2} = 6$, 1H). MS: 210 (2, $M^{\cdot+}$), 192 (7), 177 (37), 137 (35), 124 (73), 109 (85), 95 (55), 81 (77), 69 (69), 55 (72), 41 (100).

(9βH)-12-Nordriman-8α-ol (**19**). $[\alpha]_D^{20} = -6°$. ^{1}H-NMR: 0.797 (*s*, 3H), 0.868 (*s*, 3H), 0.884 (*d*, $J = 7$, 3H), 1.15 (*s*, 3H), 4.06 (*dt*, $J_1 = 12$, $J_2 = 5$, 1H). MS: 210 (0, $M^{\cdot+}$), 208 (5), 192 (13), 177 (100), 163 (11), 149 (17), 137 (42), 124 (43), 109 (56), 95 (43), 81 (51), 69 (42), 41 (48).

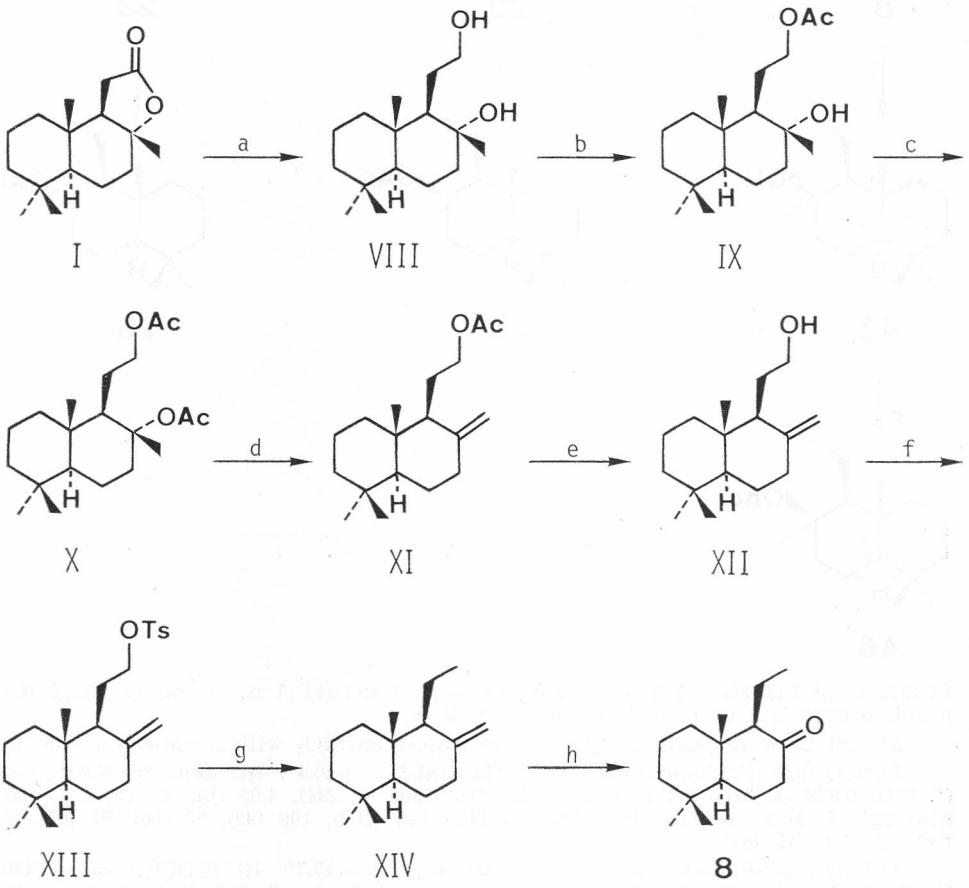
(9βH)-12-Nordriman-8β-yl Acetate (**21**). The product was crystallized from pentane: m. p. 119—120°, $[\alpha]_D^{20} = -6.2°$. ^{1}H-NMR: 0.78 (*s*, 3H), 0.81 (*s*, 3H), 0.884 (*d*, $J = 7$, 3H), 1.05 (*s*, 3H), 4.72 (*m*, $w_{1/2} = 6$, 1H). MS: 252 (0, $M^{\cdot+}$), 192 (32), 177 (45), 149 (100), 136 (31), 121 (34), 109 (40), 95 (47), 81 (56), 69 (43), 55 (45), 43 (93).

(9βH)-Driman-8β-ol (**38**). $[\alpha]_D^{20} = -19.8°$. ^{1}H-NMR: 0.84 (*s* 3H), 0.874 (*s*, 3H), 0.90 (*d*, $J = 7$, 3H), 1.175 (*s*, 3H), 1.28 (*s*, 3H). MS: 224 (4, $M^{\cdot+}$), 206 (22), 191 (62), 177 (23), 153 (18), 137 (28), 121 (33), 109 (78), 97 (65), 83 (62), 71 (100), 55 (63), 43 (77).

(9βH)-Driman-8β-yl Acetate (**40**). $[\alpha]_D^{20} = -9°$. ^{1}H-NMR: 0.773 (*s*, 3H), 0.87 (*s*, 3H), 0.90 (*d*, $J = 7$, 3H), 1.09 (*s*, 3H), 1.46 (*s*, 3H), 1.98 (*s*, 3H). MS: 266 (0, $M^{\cdot+}$), 206 (53), 191 (100), 177 (7), 163 (14), 150 (22), 137 (36), 121 (51), 109 (82), 95 (67), 82 (47), 69 (40), 55 (37), 43 (67).

Preparation of Compound 8.

Scheme 7

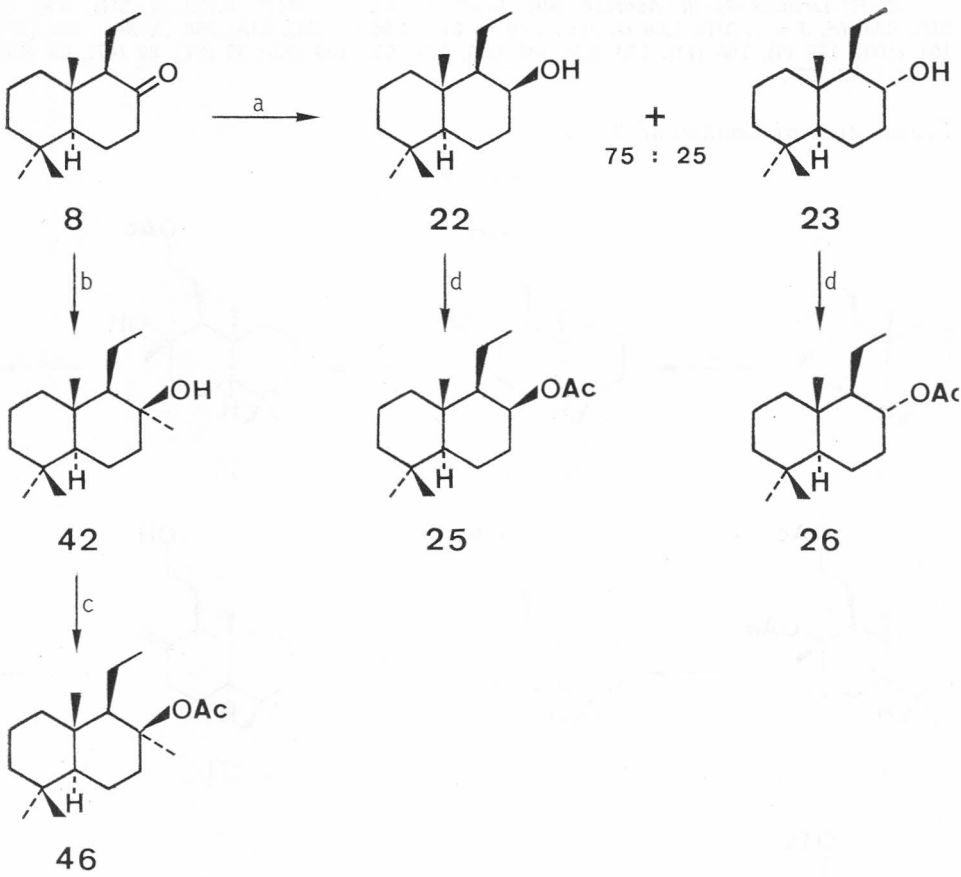


Reagents: a) $LiAlH_4$, ether/reflux/5 h; b) $(Ac)_2O$, pyridine/RT./4 h; c) $(Ac)_2O$, CH_3COCl/pyridine/40°/8 h[14]; d) N_2-stream, 300°; e) NaOH, MeOH/reflux/1 h; f) TsCl, pyridine/-70° → RT.; g) Al(*i*-Bu)$_2$H, toluene/-75° → RT.[15]; h) O_3, AcOEt/-10°, than $(Me)_2S$ added → RT./5 h.

13,14,15,16,20-Pentanorlabdan-8-one (**8**). The product was purified by chromatography on SiO_2 with hexane/ether 4 : 1. $[\alpha]_D^{20} = -58.3°$. IR: 1705. ^{1}H-NMR: 0.70 (*s*, 3H), 0.81 (*t*, $J = 7$, 3H), 0.83 (*s*, 3H), 0.97 (*s*, 3H). MS: 222 (49, $M^{\cdot+}$), 207 (15), 137 (76), 123 (63), 109 (40), 95 (58), 81 (70), 69 (77), 55 (82), 41 (100).

Preparation of Compounds **22**, **23**, **25**, **26**, **42** *and* **46**.

Scheme 8



Reagents: a) $LiAlH_4$, ether/reflux/1 h; b) MeLi, ether/RT./1 h; c) $(Ac)_2O$, CH_3COCl/pyridine/40°/5 h[14]; d) $(Ac)_2O$, pyridine/RT./20 h.

22 and **23** were purified by chromatography on SiO_2 with hexane/ether 85 : 15.

13,14,15,16,20-Pentanorlabdan-8β-ol (**22**). $[\alpha]_D^{20} = +20.4°$. IR: 3440. ^{1}H-NMR: 0.85 (*s*, 3H), 0.878 (*s*, 3H), 0.911 (*t*, $J = 7.5$, 3H), 0.985 (*s*, 3H), 4.05 (br. *s*. $w_{1/2} = 8$, 1H). MS: 224 (7, $M^{\cdot+}$), 206 (17), 191 (40), 137 (42), 124 (100), 109 (92), 95 (56), 81 (67), 69 (76), 55 (73), 41 (81).

13,14,15,16,20-Pentanorlabdan-8α-ol (**23**). $[\alpha]_D^{20} = -17.7°$. IR ($CDCl_3$): 3620, 3450. ^{1}H-NMR: 0.76 (*s*, 3H), 0.78 (*s*, 3H), 0.84 (*s*, 3H), 1.1 (*t*, $J = 7$, 3H), 3.55 (*m*, $w_{1/2} = 20$, 1H). MS: 224 (1, $M^{\cdot+}$), 206 (50), 191 (44), 137 (96), 124 (80), 109 (92), 95 (69), 81 (80), 69 (94), 55 (94), 41 (100).

13,14,15,16,20-Pentanorlabdan-8β-yl Acetate (**25**). **25** was crystallized from pentane: m. p. 90.5—92°, $[\alpha]_D^{20} = +59.8°$. IR ($CDCl_3$): 1730. ^{1}H-NMR: 0.845 (*t*, $J = 7.5$, 3H), 0.857 (*s*, 3H), 0.875 (*s*, 3H), 0.953 (*s*, 3H), 2.04 (*s*, 3H), 5.14 (*m*, $w_{1/2} = 6$, 1H). MS: 266 (0, $M^{\cdot+}$), 206 (30), 191 (42), 177 (19), 136 (57), 124 (82), 109 (47), 95 (41), 81 (51), 69 (52), 55 (51), 43 (100).

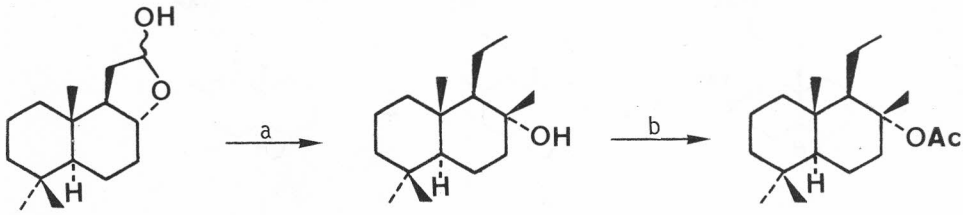
13,14,15,16,20-Pentanorlabdan-8α-yl Acetate (**26**). $[\alpha]_D^{20} = -16.5°$. IR: 1740. ^{1}H-NMR: 0.82 (*s*, 3H), 0.83 (*s*, 3H), 0.88 (*s*, 3H), 1.02 (*t*, $J = 7$, 3H), 2.04 (*s*, 3H), 4.7 (*m*, $w_{1/2} \approx 20$, 1H). MS: 266 (0, $M^{\cdot+}$), 206 (<1), 166 (33), 67 (78), 55 (100), 41 (71).

13,14,15,16-Tetranorlabdan-8β-ol (**42**). **42** was purified by chromatography on SiO_2 with hexane/ether 9 : 1. $[\alpha]_D^{20} = +8°$. IR ($CDCl_3$): 3620, 3480. ^{1}H-NMR: 0.83 (*s*, 3H), 0.85 (*s*, 3H), 0.84 (*s*, 3H), 0.98 (*t*, $J = 7$, 3H), 1.14 (*s*, 3H). MS: 238 (30, $M^{\cdot+}$), 223 (6), 220 (7), 205 (23), 117 (19), 137 (21), 109 (48), 97 (62), 85 (87), 69 (85), 55 (76), 43 (100).

13,14,15,16-Tetranorlabdan-8β-yl Acetate (**46**). $[\alpha]_D^{20} = -39.5°$. IR: 1735. ^{1}H-NMR: 0.83 (*s*, 3H), 0.88 (*s*, 3H), 0.92 (*s*, 3H), 0.99 (*t*, $J = 7$, 3H), 1.52 (*s*, 3H), 1.99 (*s*, 3H). MS: 280 (0, $M^{\cdot+}$), 220 (27), 205 (20), 137 (25), 124 (35), 109 (56), 96 (100), 81 (53), 69 (44), 55 (52), 43 (78).

Preparation of Compounds **41** *and* **45**.

Scheme 9



II 41 45

Reagents: a) NaOH, $(NH_2)_2 \cdot H_2O$/diethylene glycol → 190° [9]; b) $(Ac)_2O$, CH_3COCl/pyridine[14].

13,14,15,16-Tetranorlabdan-8α-ol (**41**). **41** was purified by chromatography on SiO_2 with cyclohexane/ether 9 : 1. $[\alpha]_D^{20} = 0°$. IR ($CDCl_3$): 3620, 3460. ^{1}H-NMR: 0.78 (*s*, 3H), 0.79 (*s*, 3H), 0.87 (*s*, 3H), 1.01 (*t*, $J = 7$, 3H), 1.14 (*s*, 3H). MS: 238 (9, $M^{\cdot+}$), 220 (5), 205 (14), 177 (8), 137 (24), 123 (20), 109 (41), 97 (52), 85 (69), 69 (79), 55 (67) 43 (100).

13,14,15,16-Tetranorlabdan-8α-yl Acetate (**45**). $[\alpha]_D^{20} = +26.5°$. IR: 1735. ^{1}H-NMR: 0.77 (*s*, 3H), 0.81 (*s*, 3H), 0.87 (*s*, 3H), 1.0 (*t*, $J = 7$, 3H), 1.43 (*s*, 3H), 1.92 (*s*, 3H). MS: 280 (0, $M^{\cdot+}$), 220 (19) 205 (20), 191 (15), 137 (50), 123 (25), 109 (57), 96 (50), 81 (57), 69 (51), 55 (100), 41 (80).

Preparation of Compounds **9**, **24**, **27**, **44** *and* **48**.

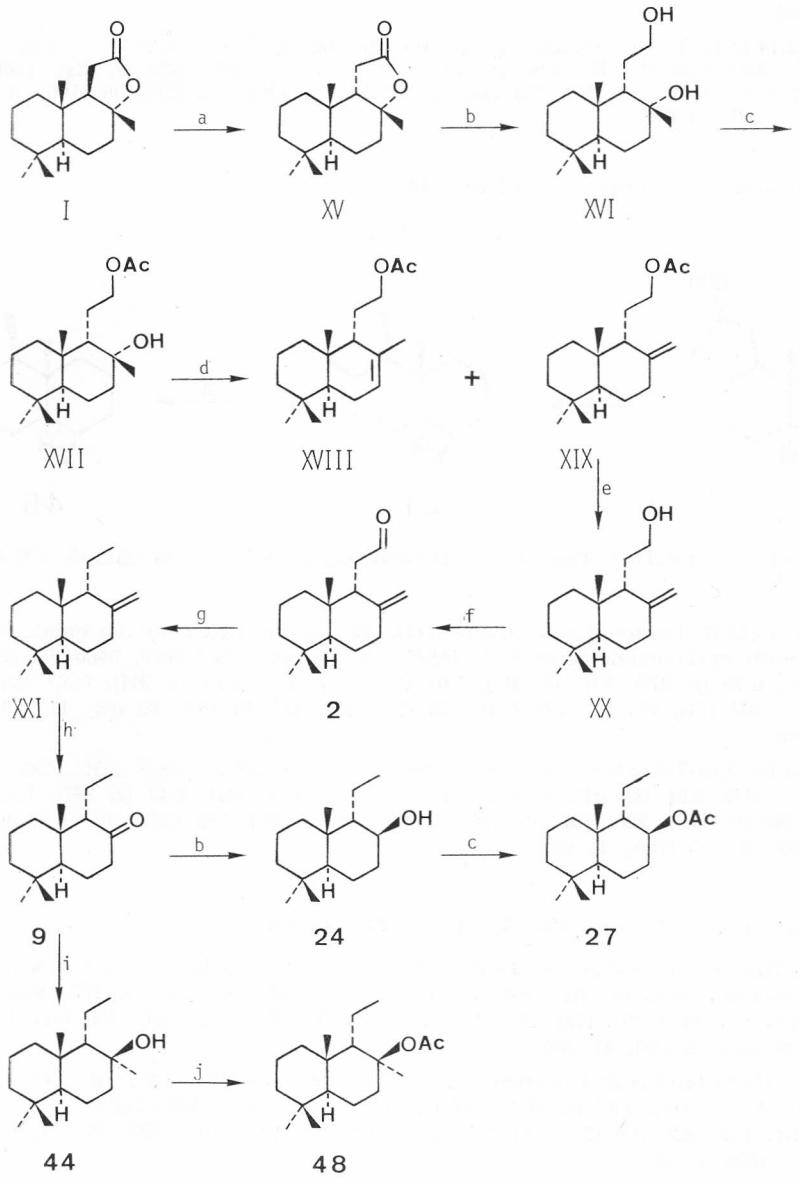
(9βH)-13,14,15,16-Tetranorlabdan-8(20)-en-12-al (**2**). $[\alpha]_D^{20} = +33.1°$. IR: 2730, 1730, 900. ^{1}H-NMR: 0.83 (*s*, 3H), 0.92 (*s*, 3H), 1.01 (*s*, 3H), 4.7 (br. *s*, 2H), 9.63 (*m*, 1H). MS: 234 (10, $M^{\cdot+}$), 219 (13), 201 (8), 190 (44), 137 (100), 123 (46), 109 (31), 95 (42), 81 (53), 69 (62), 55 (39), 41 (60).

(9βH)-13,14,15,16,20-Pentanorlabdan-8-one (**9**). $[\alpha]_D^{20} = -8.9°$. IR: 1710. ^{1}H-NMR: 0.80 (*t*, $J = 7$, 3H), 0.87 (*s*, 3H), 0.93 (*s*, 3H), 0.96 (*s*, 3H). MS: 222 (62, $M^{\cdot+}$), 207 (18), 189 (18), 179 (22), 166 (23), 151 (24), 137 (100), 123 (77), 109 (50), 95 (67), 81 (73), 69 (86), 55 (82), 41 (92).

(9βH)-13,14,15,16,20-Pentanorlabdan-8β-ol (**24**). M. p. 104—105°, $[\alpha]_D^{20} = -44.4°$. IR ($CDCl_3$): 3630, 3460. ^{1}H-NMR: 0.84 (*s*, 3H), 0.859 (*s*, 3H), 0.917 (*t* $J = 7$, 3H), 1.24 (*s*, 3H), 3.98 (br. *s*, 1H). MS: 224 (2,$M^{\cdot+}$), 206, (10), 191 (31), 137 (43), 124 (100), 109 (83), 95 (52), 81 (61), 69 (67), 55 (63), 41 (69).

(9βH)-13,14,15,16,20-Pentanorlabdan-8β-yl Acetate (**27**). $[\alpha]_D^{20} = -23.6°$. IR ($CDCl_3$): 1725. ^{1}H-NMR: 0.842 (*s*, 3H), 0.865 (*s*, 3H), 0.974 (*t*, $J = 7$, 3H), 1.133 (*s*, 3H),

Scheme 10



Reagents: a) HCOOH (98%), conc. H_2SO_4/90°/8 h[9]; b) $LiAlH_4$, ether/reflux/1 h; c) $(Ac)_2O$, pyridine/RT./8 h; d) $POCl_3$, pyridine/-20° → RT.; e) NaOH, MeOH/reflux/1 h; f) PDC, CH_2Cl_2[16]; g) NaOH, $(NH_2)_2 \cdot H_2O$/ diethylene glycol → 109°[17]; h) O_3/AcOEt, then PPh_3/-70° → RT.; i) MeLi/ether; after 60 h at RT. only 60% transformation; j) $(Ac)_2O$, CH_3COCl/pyridine/40°/8 h[14].

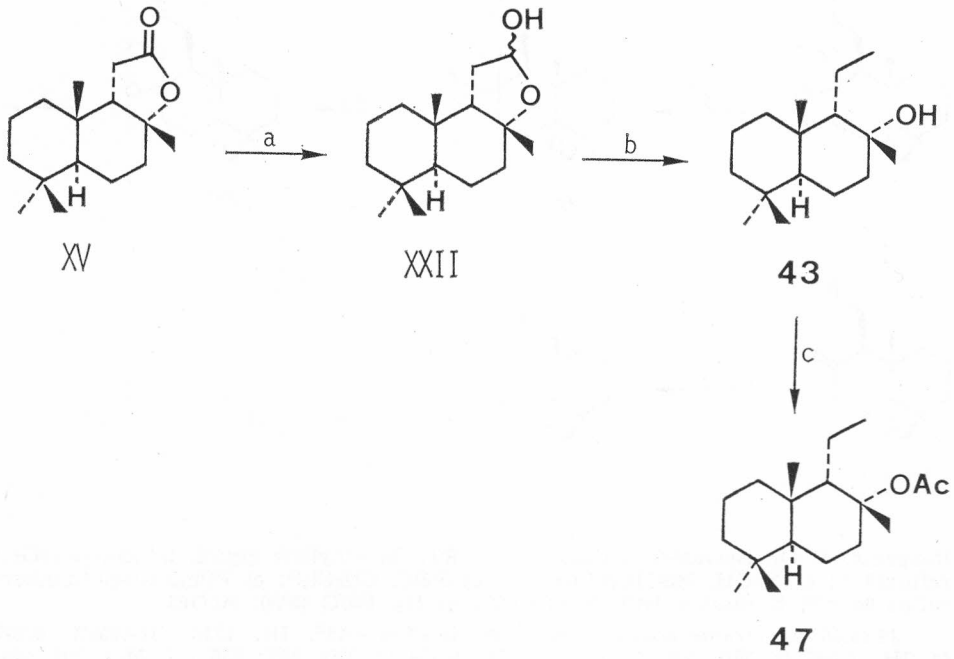
2.03 (*s*, 3H), 4.97 (*m*, $w_{1/2} = 5$, 1H). MS: 266 (0, $M^{\cdot+}$), 206 (50), 191 (57), 177 (55), 149 (55), 136 (56), 121 (40), 109 (55), 95 (51), 81 (57), 69 (64), 55 (56), 43 (100).

(9βH)-13,14,15,16-Tetranorlabdan-8β-ol (**44**). M. p. 70°, $[\alpha]_D^{20} = -25°$. IR ($CDCl_3$): 3620, 3450. ^{1}H-NMR: 0.827 (*s*, 3H), 0.856 (*s*, 3H), 0.933 (*t*, $J = 7.5$, 3H), 1.245 (*s*, 3H), 1.265 (*s*, 3H). MS: 238 (10, $M^{\cdot+}$), 220 (12), 205 (30), 177 (23), 137 (30), 123 (35), 109 (85), 97 (61), 81 (93), 69 (100), 55 (89), 43 (91).

(9βH)-13,14,15,16-Tetranorlabdan-8β-yl Acetate (**48**). $[\alpha]_D^{20} = -4.6°$. IR ($CDCl_3$): 1720. ^{1}H-NMR: 0.815 (*s*, 3H), 0.885 (*s*, 3H), 0.972 (*t*, $J = 7$, 3H), 1.09 (*s*, 3H), 1.53 (*s*, 3H), 1.975 (*s*, 3H). MS: 280 (0,$M^{\cdot+}$), 220 (10), 205 (13), 191 (19), 137 (33), 109 (78), 96 (57), 81 (71), 69 (53), 55 (67), 41 (100).

Preparation of Compounds **43** *and* **47**.

Scheme 11



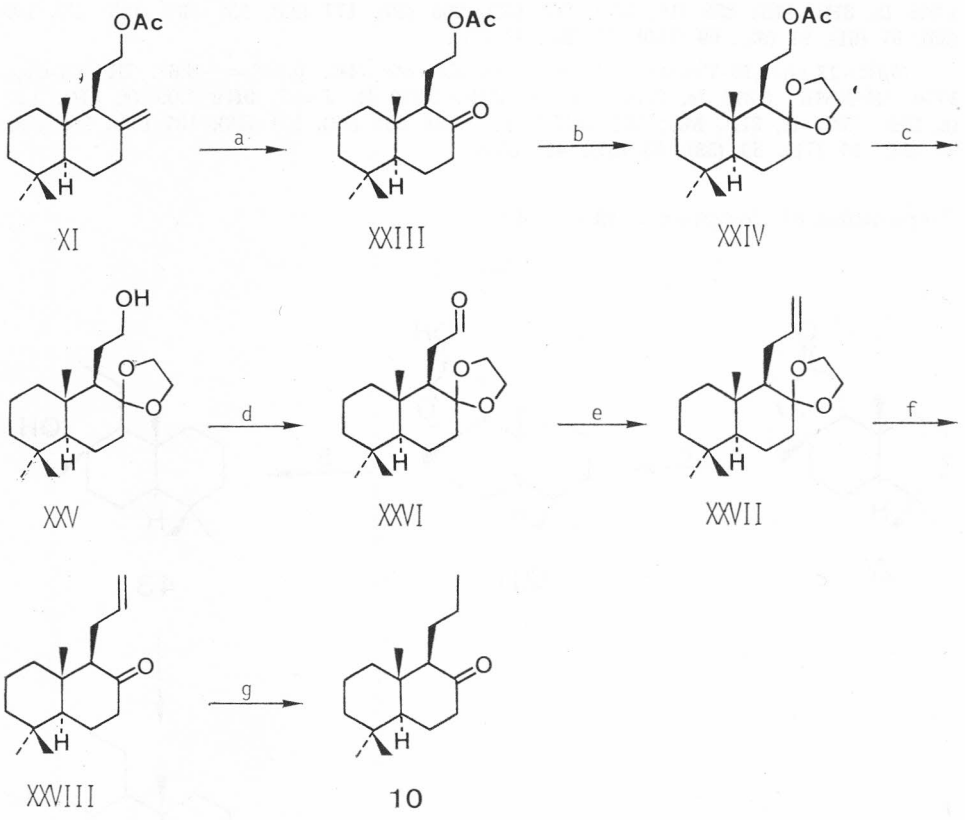
Reagents: a) Al(*i*-Bu)$_2$H, toluene/-70° [13], b) NaOH, $(NH_2)_2 \cdot H_2O$/diethylene glycol → 190° [17]; c) $(Ac)_2O$, CH_3COCl/pyridine/40°/5 h[14].

(9βH)-13,14,15,16-Tetranorlabdan-8α-ol (**43**). The product was purified by chromatography on SiO_2 with cyclohexane/ether 4 : 1. $[\alpha]_D^{20} = -26°$. IR: 3450. ^{1}H-NMR: 0.78 (*s*, 3H), 0.86 (*s*, 3H), 0.94 (*t*, $J = 7$, 3H), 1.07 (*s*, 3H), 1.44 (*s*, 3H). MS: 238 (14, $M^{\cdot+}$), 220 (16), 205 (23), 177 (21), 137 (66), 123 (35), 111 (59), 97 (81), 85 (100), 69 (99), 55 (80), 43 (91).

(9βH)13,14,15,16-Tetranorlabdan-8α-yl Acetate (**47**). $[\alpha]_D^{20} = +8.73°$. IR: 1740. ^{1}H-NMR: 0.80 (*s*, 3H), 0.88 (*s*, 3H), 1.0 (*t*, $J = 7$, 3H), 1.1 (*s*, 3H), 1.72 (*s*, 3H), 1.99 (*s*, 3H) MS: 280 (0,$M^{\cdot+}$), 220 (2), 205 (1), 182 (16), 137 (16), 126 (43), 109 (27), 99 (27), 82 (37), 69 (35), 57 (76), 43 (100).

Preparation of Compound **10**.

Scheme 12



Reagents: a) O_3, AcOEt/-70°, than $PPh_3 \rightarrow$ RT.; b) ethylene glycol, toluene/*p*-TsOH/reflux/5 h; c) NaOH, MeOH/reflux/1 h; d) PDC, CH_2Cl_2[16]; e) PPh_3MeJ-BuLi/ether/reflux/60 h[18]; f) diluted HCl, MeOH/RT.; g) H_2, Pd/C (5%), AcOEt.

14,15,16,20-Tetranorlabdan-8-one (**10**). $[\alpha]_D^{20} = -44°$. IR: 1710. ^{1}H-NMR: 0.707 (*s*, 3H), 0.845 (*s*, 3H), 0.87 (*t*, $J = 7$, 3 H), 0.978 (*s*, 3H). MS: 236 (27, $M^{\cdot+}$), 207 (25), 179 (90), 137 (53), 123 (42), 109 (33), 95 (50), 81 (61), 69 (70), 55 (100), 41 (97).

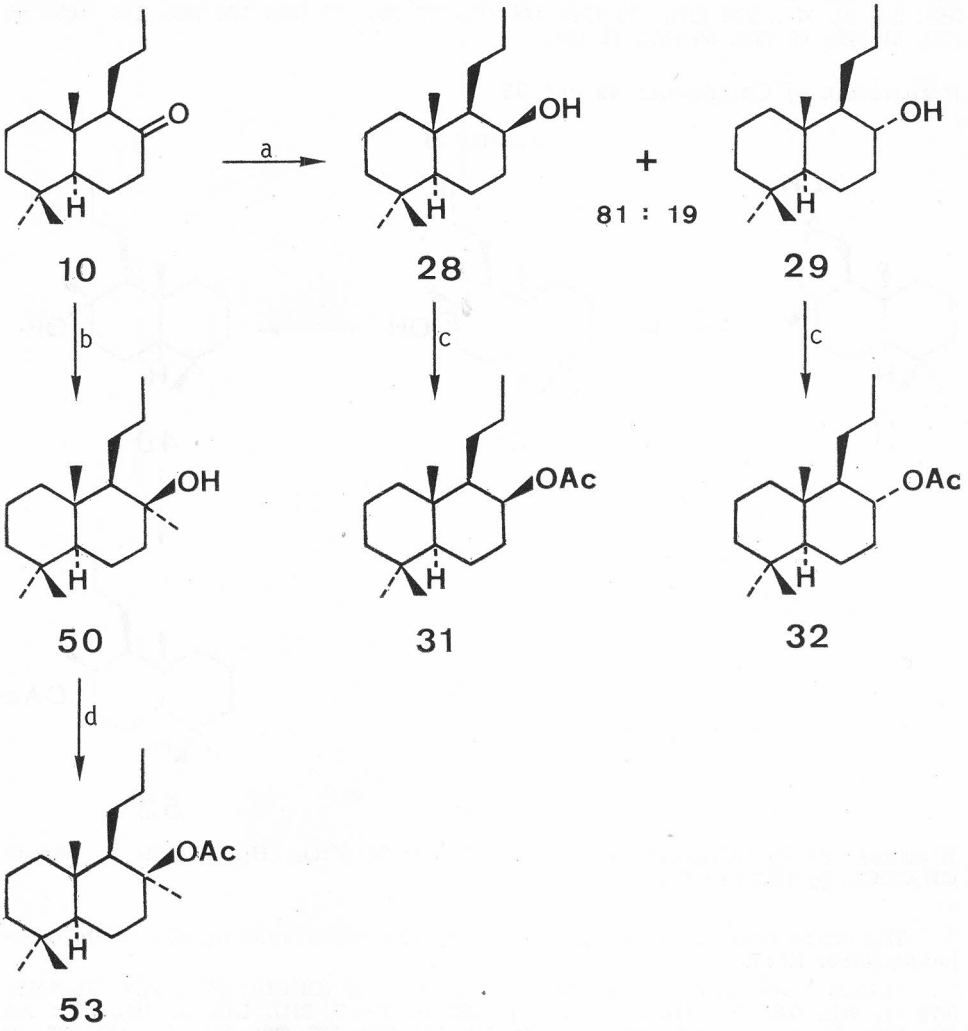
Preparation of Compounds **28**, **29**, **31**, **32**, **50** *and* **53**.

The two alcohols **28** and **29** were separated by chromatography on SiO_2 with cyclohexane/ether 96 : 4.

14,15,16,20-Tetranorlabdan-8β-ol (**28**). $[\alpha]_D^{20} = +34.4°$. IR ($CDCl_3$): 3640, 3480. ^{1}H-NMR: 0.84 (*s*, 3H), 0.865 (*s*, 3H), 0.905 (*t*, $J = 7$, 3H), 0.975 (*s*, 3H), 3.97 (*m*, $w_{1/2} = 8$, 1H). MS: 238 (4, $M^{\cdot+}$), 220 (7), 205 (30), 137 (35), 124 (93), 109 (91), 95 (49), 81 (65), 69 (90), 55 (85), 41 (100).

14,15,16,20-Tetranorlabdan-8α-ol (**29**). $[\alpha]_D^{20} = -10.2°$. IR ($CDCl_3$): 3620, 3450. ^{1}H-NMR: 0.79 (*s*, 3H), 0.77 (*s*, 3H), 0.86 (*s*, 3H), 0.89 (*t*, $J = 7$, 3H), 3.44 (*m*, $w_{1/2} = 20$, 1H). MS: 238 (0, $M^{\cdot+}$), 220 (4), 205 (5), 137 (26), 124 (21), 109 (100), 95 (13), 81 (25), 67 (50), 55 (37), 43 (76).

Scheme 13



Reagents: a) $LiAlH_4$, ether/reflux/3 h; b) MeMgI, ether/reflux/3 h; c) $(Ac)_2O$, pyridine/RT./18 h; d) $(Ac)_2O$, CH_3COCl/pyridine/40°/5 h [14].

14,15,16,20-Tetranorlabdan-8β-yl Acetate (**31**). $[\alpha]_D^{20} = +64.6°$. IR: 1730. ^{1}H-NMR: 0.855 (*s*, 3H), 0.875 (*s*, 3H), 0.86 (*t*, $J = 7$, 3H), 0.955 (*s*, 3H), 2.04 (*s*, 3H), 5.07 (*m*, $w_{1/2} = 8$, 1H). MS: 280 (0, $M^{\cdot+}$), 220 (44), 205 (56), 177 (34), 136 (80), 124 (100), 109 (55), 96 (45), 81 (54), 69 (58), 55 (96), 43 (94).

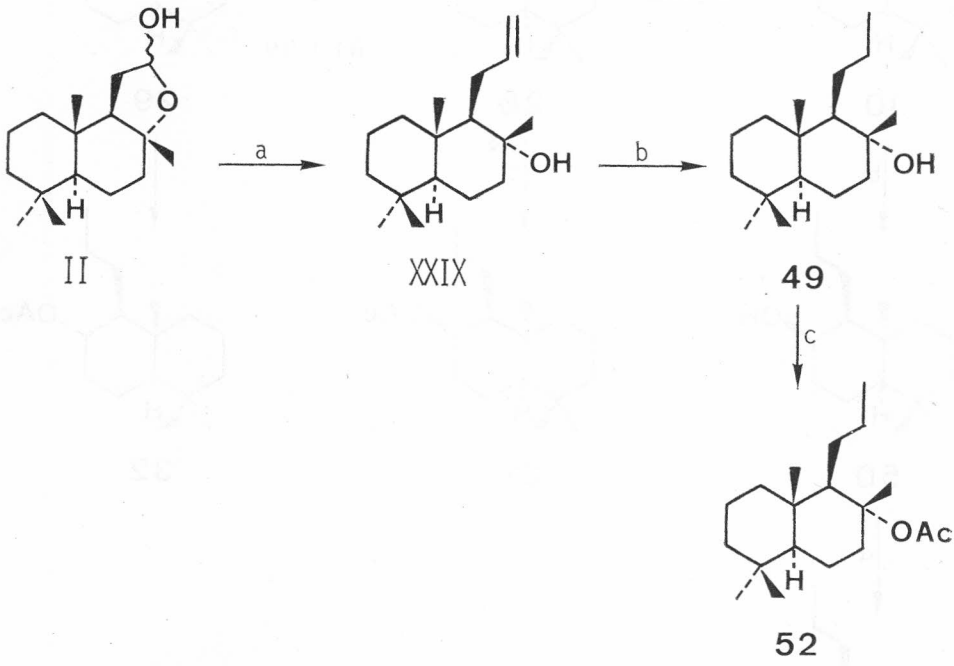
14,15,16,20-Tetranorlabdan-8α-yl Acetate (**32**). $[\alpha]_D^{20} = -18°$. IR: 1740. ^{1}H-NMR: 0.79 (*s*, 3H), 0.81 (*s*, 3H), 0.84 (*t*, $J = 7$, 3H), 0.855 (*s*, 3H). 2.0 (*s*, 3H), 4.72 (*m*, 1H). MS: 280 (1, $M^{\cdot+}$), 220 (40), 205 (48), 177 (31), 137 (67), 124 (70), 109 (50), 95 (43), 81 (54), 69 (55), 55 (62), 43 (100).

14,15,16-Trinorlabdan-8β-ol (**50**). $[\alpha]_D^{20} = +10.2°$. IR ($CDCl_3$): 3630, 3470. ^{1}H-NMR: 0.83 (*s*, 3H), 0.88 (*s*, 3H), 0.91 (*t*, $J = 7$, 3H), 0.96 (*s*, 3H), 1.13 (*s*, 3H), MS: 252 (32, $M^{\cdot+}$), 237 (6), 234 (8), 219 (32), 205 (21), 195 (20), 177 (32), 137 (33), 125 (43), 109 (46), 99 (92), 81 (53), 69 (100), 55 (70), 43 (86).

14,15,16-Trinorlabdan-8β-yl Acetate (**53**). $[\alpha]_D^{20} = +37°$. IR ($CDCl_3$): 1725. ^{1}H-NMR: 0.82 (*s*, 3H), 0.85 (*t*, $J = 7$, 3H), 0.87 (*s*, 3H), 0.91 (*s*, 3H), 1.48 (*s*, 3H), 1.98 (*s*, 3H). MS: 294 (0, $M^{\cdot+}$), 234 (21), 219 (14), 191 (7), 177 (8), 137 (33), 124 (30), 110 (100), 95 (35), 81 (45), 69 (35), 55 (37), 43 (50).

Preparation of Compounds **49** *and* **52**.

Scheme 14



II XXIX **49** **52**

Reagents: a) PPh_3CH_3O/BuLi, ether/RT./2 h[19]; b) PtO_2, H_2, AcOEt; c) $(Ac)_2O$, CH_3COCl/. pyridine/40°/8 h[14].

The crude mixture of **49** was purified by chromatography on SiO_2 with cyclohexane/ether **93 : 7.**

14,15,16-Trinorlabdan-8α-ol (**49**). $[\alpha]_D^{20} = -4.7°$. IR ($CDCl_3$): 3620, 3470. ^{1}H-NMR: 0.79 (*s*, 3H), 0.81 (*s*, 3H), 0.88 (*s*, 3H), 0.92 (*t*, $J = 7$, 3H), 1.16 (*s*, 3H). MS: 252 (21, $M^{\cdot+}$), 234 (8), 219 (16), 205 (7), 195 (11), 177 (22), 137 (29), 125 (45), 111 (46), 99 (80), 83 (49), 69 (100), 55 (70), 43 (82).

14,15,16-Trinorlabdan-8α-yl Acetate (**52**). $[\alpha]_D^{20} = -28.3°$. IR ($CDCl_3$): 1720. ^{1}H-NMR: 0.78 (*s*, 3H), 0.82 (*s*, 3H), 0.86 (*s*, 3H), 0.89 (*t*, $J = 7$, 3H), 1.45 (*s*, 3H), 1.92 (*s*, 3H).

Preparation of Compound **11**.

(9βH)-14,15,16-Trinorlabd-8(20)-en-12-one (**4**). $[\alpha]_D^{20} = -5.2°$. IR: 1710, 885. ^{1}H--NMR: 0.815 (*s*, 3H), 0.89 (*s*, 3H), 0.97 (*s*, 3H), 4.6 and 4.67 (two br. *s*, 2H). MS: 248 (2, $M^{\cdot+}$), 233 (5), 215 (6), 190 (62), 137 (47), 109 (37), 95 (48), 81 (62), 69 (53), 55 (35), 43 (100).

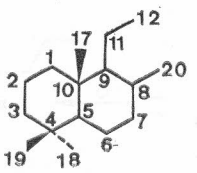
Ketone **11** was purified by prep. gas chromatography.

(9βH)-14,15,16,20-Tetranorlabdan-8-one (**11**). M. p. 67.5° $[\alpha]_D^{20} = -14.3°$. ^{1}H-NMR: 0.864 (*s*, 3H), 0.90 (*t*, $J = 7$, 3H), 0.918 (*s*, 3H), 0.964 (*s*, 3H). MS: 236 (3, $M^{\cdot+}$). 221

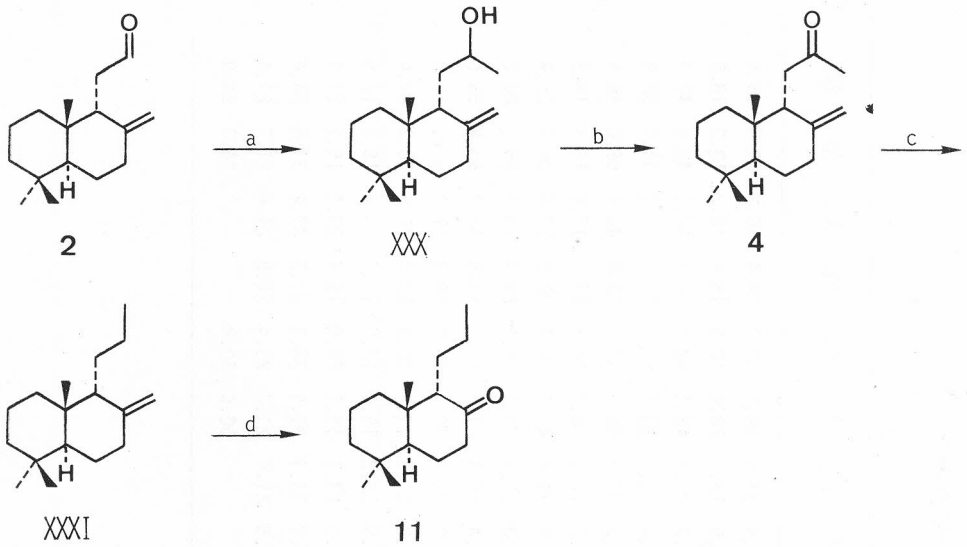
Table 1. *^{13}C-NMR chemical shifts. The δ-values are in ppm downfield from TMS*

compound / carbon	6	7	16	18	17	19	37	38	8	9	18	24	42	44	25	27	46	48
1	39.5	36.2	39.6	37.8	39.8	37.1	39.9	37.9	39.3	36.4	39.4	37.0	39.2	37.0	39.4	36.8	39.3	36.4
2	19.0	18.6	18.4	18.4	18.7	18.7	18.5	18.8	19.1	18.7	18.5	18.2	18.4	18.5	18.6	18.3	18.3	18.5
3	42.1	42.4	42.3	42.7	42.1	42.7	42.6	42.7	42.0	42.5	42.2	42.5	42.3	42.4	42.2	42.5	42.1	42.4
4	33.6	33.5	33.5	33.1	33.7	33.0	33.3	33.2	33.5	33.3	33.4	33.0	33.3	32.9	33.3	33.0	33.5	32.9
5	54.2	44.0	56.1	46.5	54.8	44.5	56.1	46.4	54.4	44.9	56.2	47.3	56.0	46.8	55.8	46.9	56.2	46.5
6	23.6	23.1	17.2	17.4	20.9	21.3	18.5	18.8	24.2	23.4	17.2	17.3	18.3	18.8	17.5	17.9	18.3	18.8
7	41.9	37.3	35.4	30.5	36.8	30.4	42.1	36.6	42.9	38.4	35.5	30.4	42.2	36.1	32.2	27.6	36.0	35.9
8	212.6	216.2	72.9	75.1	72.2	69.0	72.6	74.9	212.1	215.4	67.2	71.7	73.1	75.1	69.9	73.7	85.1	86.2
9	58.0	58.7	48.9	49.1	52.8	49.0	52.6	53.5	66.5	66.8	56.4	56.9	61.5	62.1	55.5	53.2	63.4	55.6
10	41.5	39.1	37.5	36.5	37.7	37.7	37.8	37.4	42.9	40.1	38.0	37.0	39.0	38.8	38.1	37.2	n.v.	38.9
11	6.9	13.1	11.7	14.8	10.0	6.7	7.4	12.6	24.2	20.0	17.2	21.3	17.9	22.1	17.2	20.9	18.3	21.4
12									14.1	12.0	12.9	15.2	18.0	17.5	12.7	14.4	18.1	17.5
17	13.9	22.1	15.2	23.7	13.6	22.3	14.4	24.5	14.8	22.1	16.0	23.7	15.1	24.8	15.5	23.1	15.1	23.0
18	33.5	33.5	33.7	33.6	33.6	33.4	33.6	33.5	33.7	33.5	33.8	33.4	33.5	33.3	33.7	33.4	33.5	33.4
19	21.8	22.0	21.8	22.0	21.8	21.7	21.8	22.0	21.7	22.1	21.8	21.8	21.7	21.4	21.8	21.6	21.7	21.4
20							31.0	32.4					30.6	30.9			25.3	26.0

Numbering:



Scheme 15

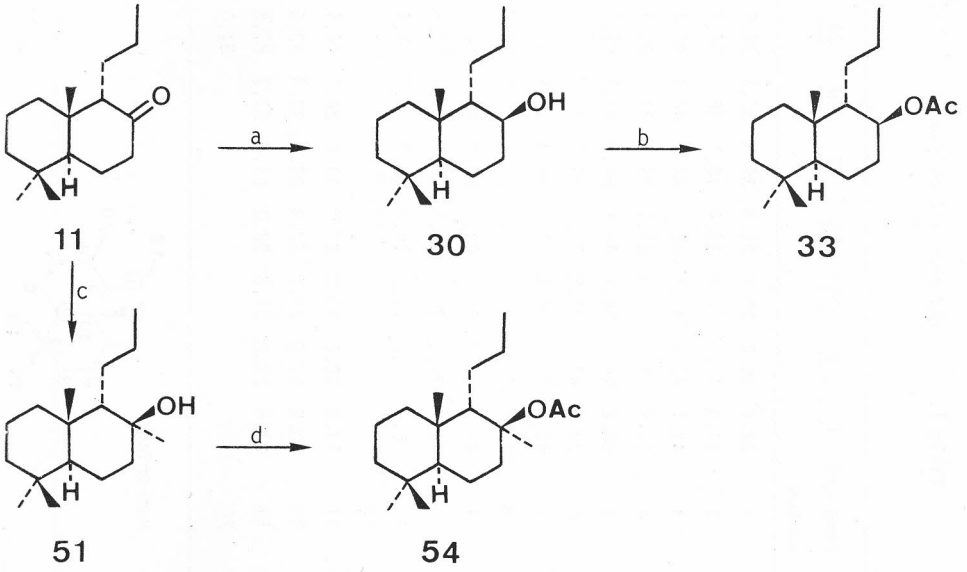


Reagents: a) MeMgI, ether/reflux/2 h; b) PDC, CH_2Cl_2[16]; c) NaOH, $(NH_2)_2 \cdot H_2O$/ diethylene glycol → 190° [17]; d) O_3, AcOEt/-70°, than PPh_3 → RT.

(3), 207 (11), 194 (37), 179 (100), 137 (39), 123 (28), 109 (30), 95 (45), 81 (53), 69 (51), 55 (82), 41 (84).

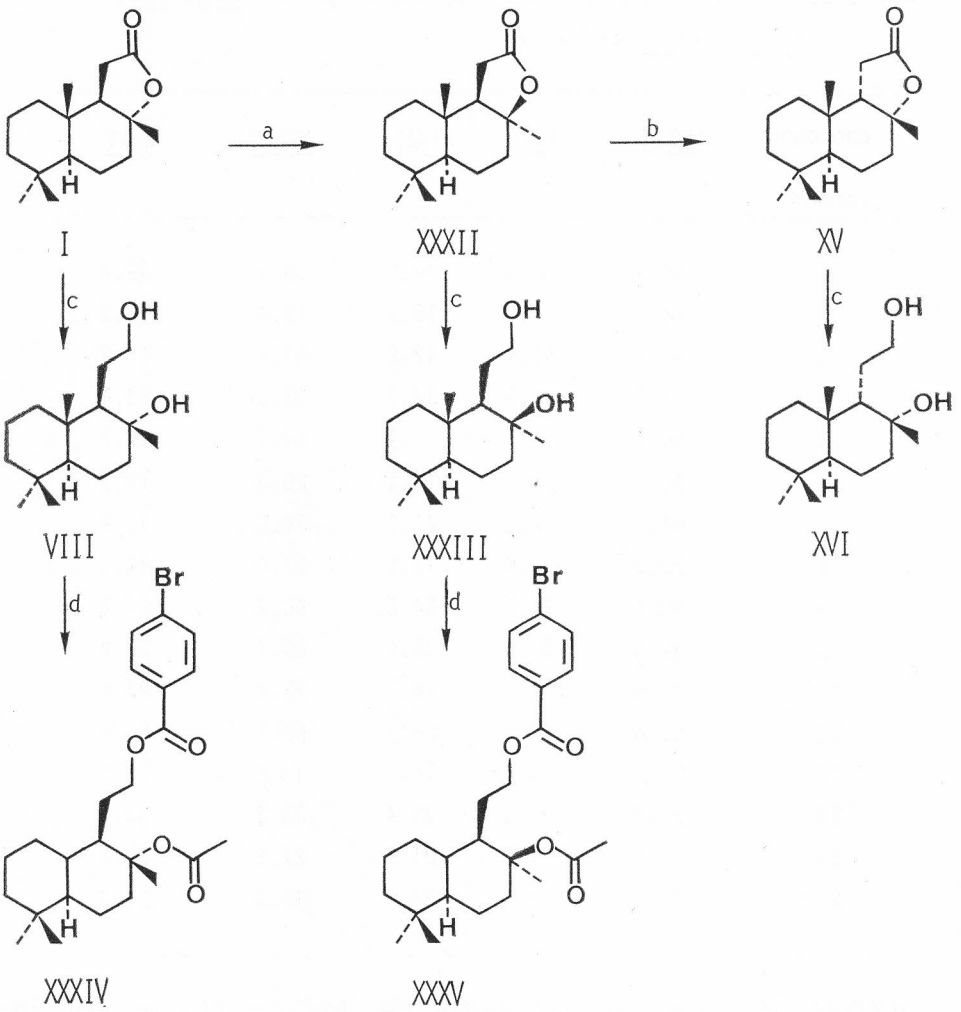
Preparation of Compounds **30**, **33**, **51** *and* **54**.

Scheme 16



Reagents: a) $NaBH_4$, EtOH/RT./4 h; b) $(Ac)_2O$, pyridine/RT./12 h; c) MeMgJ, ether/reflux/6 h; d) $(Ac)_2O$, CH_3COCl/pyridine/40°/8 h[14].

Scheme 17



Reagents: a) HCOOH (98%), conc. H_2SO_4/20°/4 h[9]: b) like a) but 95°/5 h[9]; c) $LiAlH_4$, ether/reflux/1 h; d) *p*-BrPhCOCl, pyridine/RT./20 h, then $(Ac)_2O$, CH_3COCl/pyridine/40°/18 h[14].

(9βH)-14,15,16,20-Tetranorlabdan-8β-ol (**30**). M. p. 68—69°, $[\alpha]_D^{20} = -42.4°$. IR ($CDCl_3$): 3630, 3460. ^{1}H-NMR: 0.83 (*s*, 3H), 0.855 (*s*, 3H), 0.885 (*t*, $J = 7$, 3H), 1.235 (*s*, 3H), 3.92 (*m*, $w_{1/2} = 6$, 1H). MS: 238 (1, $M^{\cdot+}$), 220 (2), 205 (8), 137 (17), 124 (53), 109 (76), 95 (38), 81 (58), 69 (61), 55 (75), 41 (100).

(9βH)-14,15,16,20-Tetranorlabdan-8β-yl Acetate (**33**). $[\alpha]_D^{20} = -23.2°$. IR: 1740. ^{1}H-NMR: 0.84 (*s*, 3H), 0.87 (*s*, 3H), 0.90 (*t*, $J = 7$, 3H), 1.12 (*s*, 3H), 2.02 (*s*, 3H), 4.91 (*m*, $w_{1/2} = 4$, 1H). MS: 280 (0, $M^{\cdot+}$), 220 (19), 205 (27), 177 (45), 149 (43), 124 (39), 109 (83), 95 (48), 81 (57), 69 (49), 55 (58), 43 (100).

(9βH)-14,15,16-Trinorlabdan-8β-ol (**51**). $[\alpha]_D^{20} = -25°$. IR ($CDCl_3$): 3620 ,3450. ^{1}H-NMR: 0.825 (*s*, 3H), 0.86 (*s*, 3H), 0.88 (*t*, $J = 7$, 3H), 1.23 (*s*, 3H), 1.26 (*s*, 3H). MS: 252 (3, $M^{\cdot+}$), 234 (5), 219 (13), 191 (7), 177 (13), 137 (28), 123 (25), 109 (54), 95 (49), 81 (63), 69 (89), 55 (77), 43 (100).

Table 2. *^{13}C-NMR chemical shifts of the compounds VIII, XVI, XXXIII, XXXIV and XXXV*

compound	VIII	XVI	XXXIII	XXXIV	XXXV
carbon					
1	39.4	37.8	39.3	39.4	39.4
2	18.5	18.6	18.3	18.4	18.2
3	41.9	42.3	42.2	41.9	41.9
4	33.3	32.9	33.3	33.2	33.4
5	56.1	46.5	55.9	55.7	55.9
6	20.5	20.8	18.1	20.3	18.2
7	44.1	36.8	41.9	38.9	35.9
8	72.7	72.9	72.9	87.0	84.5
9	59.4	58.0	54.6	55.2	57.1
10	39.0	38.6	38.5	39.1	38.9
11	27.9	29.5	28.7	25.1	24.6
12	63.8	64.2	64.9	66.7	66.8
17	15.3	24.6	15.1	15.6	15.0
18	33.5	33.1	33.4	33.3	33.4
19	21.5	21.3	21.6	21.5	21.7
20	24.5	31.9	30.7	19.9	25.5

(9βH)-14,15,16-Trinorlabdan-8β-yl Acetate (**54**). $[\alpha]_D^{20} = -11.5°$. IR: 1740. ^{1}H-NMR: 0.82 (*s*, 3H), 0.86 (*s*, 3H), 0.89 (*t*, $J = 7$, 3H), 1.075 (*s*, 3H), 1.52 (*s*, 3H), 1.97 (*s*, 3H), MS: 294 (0, $M^{\cdot+}$), 234 (13), 219 (13), 191 (27), 177 (6), 163 (6), 137 (37), 123 (27), 109 (55), 95 (56), 81 (63), 69 (54), 55 (70), 43 (100).

Preparation of Compounds **XVI**, **XXXIV** *and* **XXXV**.

The diols **VIII**, **XXXIII** and **XVI** were prepared from the corresponding lactones by reduction. Product **VIII** and **XXXIII** were further transformed into the 8-acetoxy-12-(4)-bromobenzoyl derivatives **XXXIV** and **XXXV** for the determination of stereochemistry, absolute structure and conformation by X-ray diffraction analysis. Product **XVI** was directly taken for this measurement[19].

(9βH)-13,14,15,16-Tetranorlabdane-8α,12-diol (**XVI**). M. p. 110—111°, $[\alpha_D]^{20} = -13.6°$. ^{1}H-NMR: 0.79 (*s*, 3H), 0.85 (*s*, 3H), 1.10 (*s*, 3H), 1.49 (*s*, 3H), 3.39 and 3.75 (2 *m*, 2H).

8α-Acetoxy-12-(4-bromobenzoyloxy)-13,14,15,16-tetranorlabdane (**XXXIV**). M. p. 88—90.5°, $[\alpha]_D^{20} = +2.1°$. ^{1}H-NMR: 0.79 (*s*, 3H), 0.856 (*s*, 3H), 0.872 (*s*, 3H), 1.52 (*s*, 3H), 1.95 (*s*, 3H), 2.84 (m, 1H), 4.30 (*ddd*, $J \approx 6.5$! H), 4.41 (*ddd*, $J \approx 6,5$, 1H), 7.85 (splitted *d*, $J \approx 7,5$, 2H), 7.92 (splited *d*, $J \approx 7.5$, 2H).

8β-Acetoxy-12-(4-bromobenzoyloxy)-13,14,15,16-tetranorlabdane (**XXXV**). M. p. 109—111°, $[\alpha]_D^{20} = +31.6°$. ^{1}H-NMR: 0.828 (*s*, 3H), 0.87 (*s*, 3H), 0.945 (*s*, 3H), 1.55 (*s*, 3H), 1.98 (*s*, 3H), 4.3 (*m*, 2H), 7.6 (*d/t*, $J_1 = 8$, $J_2 \approx 3$, 2H), 7.9 (*d/t*, $J_1 = 8$, $J_2 \approx 3$, 2H).

Acknowledgements. — We wish to Thank Dr. L. Weiler for providing a copy of the NMR-spectra of compound **V**, and W. Thommen and R. Brauchli for recording and assistance in interpretation of the ^{13}C-NMR spectra.

REFERENCES

1. G. Ohloff, in *Fragrance Chemistry*, E. T. Theimer Editor (Academic Press, New York, 1982), pp 535—573.
2. M. Stoll and M. Hinder, *Helv. Chim. Acta* **33** (1950) 1251.
3. G. Ohloff, W. Giersch, K. H. Schulte-Elte, and Ch. Vial, *Helv. Chim. Acta* **59** (1976) 1140.
4. G. Ohloff, F. Näf, R. Decorzant, W. Thommen, and E. Sundt, *Helv. Chim. Acta* **56** (1973) 1414.
5. G. Ohloff, in *Olfaction and Taste VII*, H. van der Starre Editor (IRL Press Ltd., London and Washington, 1980), pp 3—11.
6. G. Ohloff, B. Maurer, B. Winter, and W. Giersch, *Helv. Chim. Acta* **66** (1983) 192.
7. G. Ohloff, W. Giersch, W. Thommen, and B. Willhalm, *Helv. Chim. Acta* **66** (1983) 1343.
8. M. Hinder and M. Stoll, *Helv. Chim. Acta* **36** (1953) 1995.
9. G. Lucius, *Chem. Ber.* **93** (1960) 2663; see also A. Saito, H. Matsushita, Y. Tsujino, and H. Kaneko, *Chem. Lett.* (1981) 757.
10. S. W. Pelletier, S. Lajšić, Y. Ohtsuka, and Z. Djarmati, *J. Org. Chem.* **40** (1975) 1607; J. R. Hlubucek, A. J. Aasen, and S.-O. Almqvist, *Acta Chem. Scand., Ser. B* **28** (1974) 289.
11. L. Weiler provided us with NMR spectra of V; see R. J. Armstrong, F. L. Harris, and L. Weiler, *Can. J. Chem.* **60** (1982) 673.
12. R. W. Skeean, G. L. Trammell, and J. D. White, *Tetrahedron Lett.* (1976) 525.
13. J. Schmidlin and A. Wettstein, *Helv. Chim. Acta* **46** (1963) 2799.
14. G. Ohloff, *Helv. Chim. Acta* **41** (1958) 845.
15. C. G. M. Janssen, P. M. van Lier, P. Schipper, L. H. J. G. Simons, and E. F. Godefroi, *J. Org. Chem.* **45** (1980) 3159.
16. E. J. Corey and G. Schmidt, *Tetrahedron Lett.* (1979) 399.
17. Huang-Minlon, *J. Amer. Chem. Soc.* **68** (1946) 2487.
18. *Org. Synth.* **40** (1960) 66.
19. G. Bernardinelli, A. Dunand, H. D. Flack, K. Yvon, W. Giersch, and G. Ohloff, *Acta Cryst. C* **40** (1984) 1911; G. Bernardinelli and W. Giersch, *Acta Cryst. C* **41** (1985) 746.

IZVOD

Odnosi strukture i aktivnosti pri mirisnoj percepciji drimanskih derivata

Günther Ohloff i Wolfgang Giersch

Drvenast miris *trans*-dekalonskih derivata tipa **5**, sličan sivom amberu, pojačava se sa uvođenjem ekvatorijalnih alkil-supstituenata u položaj 9, a drastično slabi kod odgovarajućih 9-epi-derivata. Potpuna stereokontrola mirisne percepcije zapažena je kod diastereoizomera γ-biciklohomofarnezala **1** i **2**. Slična težnja u mirisnoj percepciji primećena je kod supstituisanih alkohola tipa **12**, ali nesumnjivo, sa neizvesnijom pravilnošću. Mirisni ton sivog ambera sličan sandalovini nađen kod »Polywood(R)« (14) iščezava u odgovarajućim alkil-supstituisanim acetatima. Molekulska osnova mirisa »steroidnog tipa« nekih estara tipa **39** do sada nije bila poznata.