Boron Trifluoride Etherate-catalyzed Backbone Rearrangement of 5α,10α-Epoxyalnusan-3β-yl Acetate and Partial Synthesis of Isomultiflorenol[1)]

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Epoxidation of alnus-5(10)-en-3β-yl acetate with *m*-chloroperbenzoic acid gave a 5α,10α-epoxide, treatment of which with boron trifluoride etherate afforded multiflora-5,8-dien-3β-yl acetate. On hydrogenation and hydrolysis, the diene gave isomultiflorenol.

In the previous paper,[2)] the boron trifluoride etherate ($BF_3 \cdot OEt_2$)-catalyzed backbone rearrangement of 5,6-epoxyalnusan-3β-yl acetate was reported. Further investigation on a behavior of carbonium ions generated on B-ring was attempted. This paper describes the epoxidation of alnus-5(10)-ene derivatives, the $BF_3 \cdot OEt_2$-catalyzed backbone rearrangement of a 5α,10α-epoxy acetate, and also a preparation of isomultiflorenol (**1**)[3-7)] from one of the rearranged products.

Alnus-5(10)-en-3β-yl acetate (**4**),[8)] prepared from dendropanoxide (**5**),[9)] was subjected to the epoxidation with *m*-chloroperbenzoic acid (MCPBA) to afford a single epoxide (**6**) in a good yield. However, no information on the configuration of the epoxide ring could be obtained from any spectrum of **6** (See Experimental).

In order to determine the configuration of the epoxide (**6**), the following epoxidation reactions were examined. Alnus-5(10)-en-3β-ol (**7**) and its benzoate (**8**) were epoxidized with MCPBA under the same conditions as above to afford single epoxides (**9** and **10**), respectively. On acetylation, the epoxide (**9**) yielded an epoxy acetate, which was identical with **6**. Treatment of **10** with lithium aluminium hydride afforded an epoxy alcohol identical with **9**. Therefore, the epoxide rings of **6**, **9**, and **10** are in all the same configurations.

Since the signals due to 3α-protons of alnus-5(10)-en-3β-ol (**7**), -3β-yl acetate (**4**), and -3β-yl benzoate (**8**) were observed as double doublets at δ 3.44 (J=10 and 4 Hz), δ 4.69 (J=10 and 4 Hz), and δ 4.94 (J=10 and 4 Hz), respectively, in the ^1H NMR spectra, the substituents at C-3β exist in an equatorial orientation. From these facts, it could be understood why the 3β-oxygen functions did not participate in these epoxidation reactions, hence the reagent attacked exclusively from the less hindered α-side of the molecule (4β- and 9β-methyl groups are perpendicular to the 5,10-double bond plane, while the 4α-methyl group lies in the plane). Therefore, the epoxide rings of **6**, **9**, and **10** were considered to be in the α-configuration.

Then, epoxidation reactions of alnus-5(10)-en-3α-*O*-derivatives were examined. In the case of these 3α-*O*-derivatives, since the substituents at C-3α exist in an axial orientation, the bulky substituents block the α-side of the molecule and the attack of the epoxidizing reagent from the α-side was considered to be hindered. Epoxidation of alnus-5(10)-en-3α-ol (**11**) and its acetate (**12**) under the same conditions as above gave single epoxides (**13** and **14**), respectively, while 3α-benzoate (**15**), on epoxidation, gave two epoxides (**16** and **17**) in a ratio of 7:1. The relative configurations of the epoxide rings of **13**, **14**, and **16** were confirmed by the derivatization as in the case of the 3β-*O*-derivatives, and proved to be in all the same. These substituent effects are explained by the steric hindrance due to 4β- and 9β-methyl groups and partly by the hydrogen bond formation between the reagent and the 3α-axial hydroxyl group in the case of **11**, resulting in the exclusive formation of the α-epoxide (**13**). In the case of the benzoate (**15**), the attack from the α-side of the molecule was sterically slightly hinderded by the bulky benzoyloxyl group to afford the β-epoxide (**17**) as the minor product, while the acetoxyl group was not large enough to prevent the attack from the α-side. Thus the configurations of the epoxide rings of **13**, **14**, and **16** are concluded to be α.

These assignments of the epoxide rings were further confirmed by the Sharpless epoxidation.[10)] Epoxidation of alnus-5(10)-en-3α-ol (**11**) with vanadyl acetylacetonate ($VO(acac)_2$) and *t*-butyl hydroperoxide afforded a single epoxide which was identical with 5α,10α-epoxide (**13**) obtained by MCPBA. However epoxidation of alnus-5(10)-en-3β-ol (**7**) with the same conditions gave a single epoxide, but it was different from the 5α,10α-epoxide (**9**) obtained by MCPBA. From the spectral data and formation mechanism, it was concluded to be a 5β,10β-epoxide (**18**).

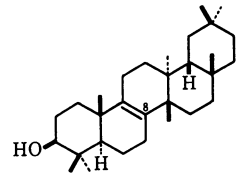
The epoxy-3β-ol (**9**), obtained by the reaction with MCPBA, was oxidized to give a keto epoxide (**19**) which was identical with that obtained by the oxidation of the epoxy-3α-ol (**13**); thus the epoxide rings of the 3β-*O*-derivatives (**6**, **9**, and **10**) and the 3α-*O*-derivatives (**13**, **14**, and **16**) are the same.

From these facts, the epoxidation reaction of these 5(10)-ene derivatives was shown to occur from the α-side of the molecule exclusively except for 5(10)-en-3α-yl benzoate (**15**). These results are opposite from those obtained for the epoxidation of alnus-5-en-3β-ol and its derivatives.[2]

The assignments of these epoxide rings were supported by the NMR spectral measurement (see Tables 1 and 2). The protons at C-3 of alnus-5(10)-en-3β-ol (**7**) and -3α-ol (**11**) resonated at nearly the same magnetic fields, while a remarkable difference in shift values due to the protons at C-3 was observed between 5α,10α-epoxy-3β-ol (**9**) and 5α,10α-epoxy-3α-ol (**13**); the 3α-H of **9** is deshielded by 0.34 ppm relative to that of **13**. This observation is ascribed to an anisotropic effect of an oxygen atom of the epoxide caused by a proximation of the 3α-axial proton of **9** to the oxygen atom.

This anisotropic effect is also observed in the ^{1}H NMR spectra of the corresponding acetates (**6** *vs.* **14**) and benzoates (**10** *vs.* **16**).

The same observations were given in the ^{1}H NMR spectral examination of 5β,10β-epoxides, although the differences are not so large, because the 3β-protons exist in an equatorial orientation. The 3β-protons of 5β,10β-epoxy-3α-ol (**20**), 5β,10β-epoxy-3α-yl acetate (**21**), and 5β,10β-epoxy-3α-yl benzoate (**17**) appeared at



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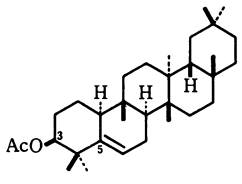

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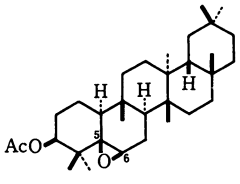

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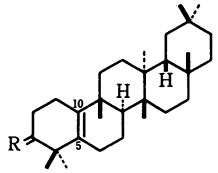
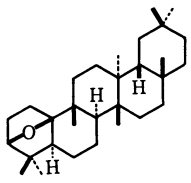


4 R=α-H, β-OAc
7 R=α-H, β-OH
8 R=α-H, β-OCOPh
11 R=α-OH, β-H
12 R=α-OAc, β-H
15 R=α-OCOPh, β-H



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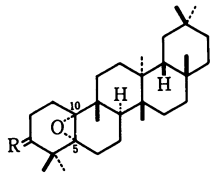
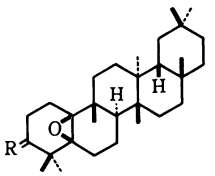
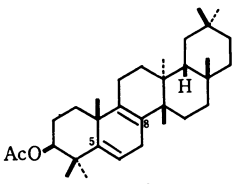


6 R=α-H, β-OAc
9 R=α-H, β-OH
10 R=α-H, β-OCOPh
13 R=α-OH, β-H
14 R=α-OAc, β-H
16 R=α-OCOPh, β-H
19 R=O



17 R=α-OCOPh, β-H
18 R=α-H, β-OH
20 R=α-OH, β-H
21 R=α-OAc, β-H
22 R=α-H, β-OAc
23 R=α-H, β-OCOPh



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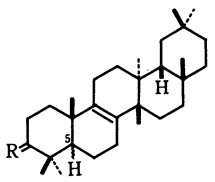

26 5α-H; R=α-H, β-OAc
27 5β-H; R=α-H, β-OAc
28 5β-H; R=α-H, β-OH
29 5α-H; R=O
30 5β-H; R=O

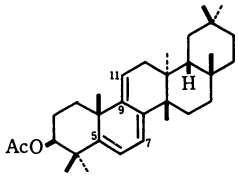

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TABLE 1. THE δ VALUES OF C-3 PROTONS OF ALNUS-5(10)-ENE DERIVATIVES AND 5,10-EPOXYALNUSANE DERIVATIVES IN THE ^{1}H NMR SPECTRA

	δ-values	
	C-3α protons of 3β-*O*- derivatives	C-3β protons of 3α-*O*- derivatives
5(10)-en-3-ol	**7** 3.44 dd J=10, 4	**11** 3.45 t-like J=4
5α,10α-epoxy-3-ol	**9** 3.58 dd J=10, 5	**13** 3.24 dt J=11, 3 3.52 d J=11 (-OH)
5β,10β-epoxy-3-ol	**18** 3.17 br s 2.71 br s (-OH)	**20** 3.41 dd J=7, 3
5(10)-en-3-yl acetate	**4** 4.69 dd J=10, 5	**12** 4.70 t J=4
5α,10α-epoxy-3-yl acetate	**6** 4.77 dd J=10, 4	**14** 4.47 dd J=7, 4
5β,10β-epoxy-3-yl acetate	**22** 4.36 dd J=11, 4	**21** 4.57 dd J=7, 3
5(10)-en-3-yl benzoate	**8** 4.94 dd J=10, 4	**15** 4.96 dd J=5, 3
5α,10α-epoxy-3-yl benzoate	**10** 5.02 dd J=11, 4	**16** 4.72 dd J=7, 3
5β,10β-epoxy-3-yl benzoate	**23** 4.62 dd J=10, 5	**17** 4.78 dd J=5.5, 3

TABLE 2. ^{13}C NMR SPECTRA OF ALNUS-5(10)-EN-3-OLS AND 5,10-EPOXYALNUSAN-3-OLS

7	11	9	13	18	20
18.6	18.6 t	16.7 t	16.7 t	15.6 t	15.9 t
18.8	18.8 q	17.2 q	18.4 q	18.1 q	18.0 q
20.5	19.0 t	18.3 q	18.6 q	18.9 q	18.9 q
20.7	20.5 q	18.7 q	19.5 t	19.9 q	19.7 t
21.0	21.2 q	19.9 q	19.8 q	20.6 t	21.1 q
23.2	23.1 q	20.6 q	21.4 q	21.0 q	21.1 q
24.7	25.9 t	23.5 t	24.1 t	24.7 t	22.6 q
27.0	27.0 t	24.4 t	24.2 t	25.4 q	24.5 t
27.7	28.0 q	26.1 t	25.5 q	28.1 s	28.1 s
28.2	28.2 s	28.1 s	28.2 s	29.0 t	29.5 t
30.1	30.1 t	29.0 t	28.8 t	29.9 s	30.0 s
31.0	31.0 s	30.0 s	30.1 s	31.6 q	31.7 q
31.6	31.8 t	30.2 t	30.2 t	31.8 t	31.8 s
31.8	31.8 q	31.9 q	32.0 q	32.2 t	32.2 t
32.2	32.2 q	32.1 q	32.1 q	32.2 q	32.2 q
32.3	32.4 t	32.4 t	32.4 t	32.7 t	32.6 t
32.9	32.9 t	32.9 t	32.9 t	32.9 t	32.8 t
35.1	35.1 q	34.9 q	34.9 q	35.1 q	35.2 q
35.5	35.5 t	35.3 t	35.3 t	35.5 t	35.5 t
36.1	36.1 t	36.0 t	36.0 t	35.9 t	36.0 t
37.5	37.6 s	36.9 s	36.9 s	37.6 s	37.7 s
38.3	38.3 s	37.9 s	37.1 s	37.8 s	37.8 s
39.4	38.8 s	38.6 s	37.9 s	38.8 s	38.8 s
39.4	39.4 t	* 38.8 d	* 38.7 d	39.4 t	39.4 t
39.5	39.5 s	39.2 t	39.2 t	39.4 s	39.5 s
42.8	42.8 d	39.3 s	39.3 s	42.6 d	42.7 d
* 47.9	* 47.8 d	42.9 d	42.9 d	* 49.6 d	* 49.7 d
** 76.2	** 75.5 d	71.0 s	71.4 s	71.8 s	69.7 s
131.7	130.0 s	71.9 s	73.3 s	73.6 s	** 72.7 d
137.3	137.4 s	** 72.2 d	** 76.5 d	** 76.5 d	72.8 s

* Assignable to C-8. ** Assignable to C-3.

lower fields than the 3α-protons of the corresponding 3β-alcohol (**18**), 3β-acetate (**22**), and 3β-benzoate (**23**), respectively.

In the ^1H NMR spectra of **13** and **18**, signals due to hydroxyl protons were observed at δ 3.52 and 2.71, respectively. Appearance of these signals is ascribed to the formation of hydrogen bond between the epoxide oxygen atom and the hydroxyl proton, resulting in the retardation of the exchange rate of the hydroxyl proton. This observation also supports the assignment of the epoxides, because the hydrogen bond could not be formed in 5α,10α-epoxy-3β-ol (**9**) nor 5β,10β-epoxy-3α-ol (**20**).

In the ^{13}C NMR spectrum of α-epoxy-3β-ol (**9**), a signal due to C-3 atom to which the proton resonating in a low field (δ 3.58) was attached, was observed in a higher field by 3.3 ppm than that of C-3 atom of α-epoxy-3α-ol (**13**). In the ^{13}C NMR spectra of β-epoxy alcohols, it was shown that C-3 atom of 3α-alcohol (**20**) resonated in a higher field relative to that of 3β-alcohol (**18**).

From the same reason, it is understood that C-8 atoms, bearing hydrogen atoms in α-orientation, of α-epoxides (**9** and **13**) resonate in a higher field by *ca.* 9 ppm than those of 5(10)-en-3-ols (**7** and **11**), while C-8 atoms of β-epoxides (**18** and **20**) resonates at nearly the same magnetic field as 5(10)-en-3-ols.

These observations described above are strongly indicative of the correct assignment of the epoxide rings.

The unequivocal proof for the structure of 5α,10α-epoxyalnusan-3β-yl acetate (**6**) was provided by X-ray single crystal analysis. The crystals of **6** belong to a monoclinic space group C_2, and the lattice parameters are a=13.446(4), b=6.739(2), c=32.257(7) Å, and β=103.71(3)°; z=4. Intensity data were measured on a Philips PW1100 automatic four-circle diffractometer using monochromated Cu $K\alpha$ radiation. A total of 2951 independent reflections with $F_o \geqq 2.5\sigma(F_o)$ were obtained by $2\theta-\theta$ scanning mode. The structure was solved by the direct method using the MULTAN 80 program and was refined by the block-diagonal least squares method. All hydrogen atoms were located on a difference electron density map. The final R-value was 0.056 assuming the anisotropic temperature factors for the non-hydrogen atoms and the isotropic ones

for the hydrogen atoms. The final atomic coordinates are listed in Table 3 and bond lengths and bond angles are listed in Tables 4 and 5.[11] Figure 1 is a computer-generated perspective drawing of the molecule of 5α,10α-epoxyalnusan-3β-yl acetate (**6**).

5α,10α-Epoxyalnusan-3β-yl acetate (**6**) was treated with $BF_3 \cdot OEt_2$ (1.2 equiv) in benzene to afford a reaction mixture, which was shown to consist of a main product (**24**; *ca.* 80% yield) and more than seven minor components by HPLC examination. The reaction mixture was subjected to separation by column chromatography to give the pure main product (**24**), $C_{32}H_{50}O_2$ (determined by the high-resolution mass spectrum), showed no chracteristic absorption maxi-

Table 3. Atomic positional parameters (×10⁴) and isotropic temperature factors (×10²) for non-hydrogen atoms of 5α, 10α-epoxyalnusan-3β-yl acetate (**6**) with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}[a]	Atom	x	y	z	B_{eq}[a]
C(1)	3874 (2)	2605 (0)	1572 (1)	422 (6)	C(19)	6057 (3)	69 (7)	3862 (1)	460 (6)
C(2)	3564 (3)	3303 (6)	1111 (1)	395 (5)	C(20)	6432 (3)	−918 (8)	4300 (1)	523 (7)
C(3)	4317 (3)	4817 (5)	1017 (1)	361 (5)	C(21)	7585 (3)	−421 (10)	4482 (1)	633 (9)
C(4)	5408 (3)	4000 (6)	1075 (1)	377 (5)	C(22)	8037 (3)	880 (9)	4179 (1)	571 (7)
C(5)	5765 (2)	3210 (5)	1529 (1)	328 (4)	C(23)	6112 (3)	5711 (7)	1010 (1)	530 (7)
C(6)	6882 (3)	2618 (8)	1662 (1)	496 (7)	C(24)	5444 (3)	2326 (7)	753 (1)	531 (7)
C(7)	7142 (2)	1077 (7)	2018 (1)	439 (6)	C(25)	5128 (3)	−1072 (5)	1939 (1)	440 (6)
C(8)	6508 (2)	1412 (5)	2351 (1)	303 (4)	C(26)	6268 (3)	3116 (6)	3203 (1)	431 (6)
C(9)	5361 (2)	1012 (4)	2138 (1)	278 (4)	C(27)	7037 (3)	−1899 (6)	2723 (1)	457 (6)
C(10)	5018 (2)	2486 (5)	1768 (1)	289 (4)	C(28)	8459 (3)	−2047 (9)	3776 (1)	630 (8)
C(11)	4734 (2)	1340 (6)	2475 (1)	350 (5)	C(29)	6277 (4)	−3205 (10)	4262 (1)	704 (9)
C(12)	5163 (2)	259 (6)	2896 (1)	353 (5)	C(30)	5799 (4)	−68 (13)	4598 (1)	875 (14)
C(13)	6273 (2)	861 (5)	3108 (1)	297 (4)	C(31)	3496 (3)	7192 (6)	496 (1)	451 (6)
C(14)	6954 (2)	367 (5)	2788 (1)	323 (4)	C(32)	3252 (5)	7673 (9)	22 (1)	766 (10)
C(15)	8049 (2)	1158 (8)	2972 (1)	487 (6)	O(1)	5461 (2)	4458 (3)	1846 (1)	373 (3)
C(16)	8386 (3)	1346 (8)	3461 (1)	559 (7)	O(2)	3962 (2)	5451 (4)	573 (1)	447 (4)
C(17)	7874 (2)	−46 (7)	3726 (1)	428 (6)	O(3)	3298 (3)	8235 (6)	764 (1)	728 (7)
C(18)	6687 (2)	−328 (5)	3530 (1)	342 (5)					

a) $B_{eq} = 8\pi(u_1^2 + u_2^2 + u_3^2)/3$.

Table 4. Bond lengths (*l*/Å) of 5α,10α-epoxyalnusan-3β-yl acetate (**6**) with estimated standard deviations in parentheses

Bond length		(*l*/Å)	Bond length		(*l*/Å)
Atom 1	Atom 2		Atom 1	Atom 2	
C(1)	-C(2)	1.523 (5)	C(12)	-C(13)	1.542 (4)
C(1)	-C(10)	1.520 (4)	C(13)	-C(14)	1.569 (5)
C(2)	-C(3)	1.517 (5)	C(13)	-C(18)	1.563 (4)
C(3)	-C(4)	1.537 (5)	C(13)	-C(26)	1.550 (5)
C(3)	-O(2)	1.461 (4)	C(14)	-C(15)	1.546 (4)
C(4)	-C(5)	1.525 (4)	C(14)	-C(27)	1.549 (5)
C(4)	-C(23)	1.537 (6)	C(15)	-C(16)	1.539 (5)
C(4)	-C(24)	1.542 (6)	C(16)	-C(17)	1.537 (6)
C(5)	-C(6)	1.514 (5)	C(17)	-C(18)	1.582 (4)
C(5)	-C(10)	1.486 (5)	C(17)	-C(22)	1.557 (6)
C(5)	-O(1)	1.456 (4)	C(17)	-C(28)	1.550 (7)
C(6)	-C(7)	1.526 (6)	C(18)	-C(19)	1.538 (5)
C(7)	-C(8)	1.539 (5)	C(19)	-C(20)	1.535 (5)
C(8)	-C(9)	1.556 (4)	C(20)	-C(21)	1.558 (6)
C(8)	-C(14)	1.562 (4)	C(20)	-C(29)	1.555 (9)
C(9)	-C(10)	1.538 (4)	C(20)	-C(30)	1.539 (7)
C(9)	-C(11)	1.540 (5)	C(21)	-C(22)	1.539 (7)
C(9)	-C(25)	1.546 (5)	C(31)	-C(32)	1.520 (6)
C(10)	-O(1)	1.454 (4)	C(31)	-O(2)	1.326 (5)
C(11)	-C(12)	1.529 (4)	C(31)	-O(3)	1.193 (5)

TABLE 5. BOND ANGLES (ϕ/°) OF 5α,10α-EPOXYALNUSAN-3β-YL ACETATE (**6**) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond angle			ϕ/°	Bond angle			ϕ/°
Atom 1	Atom 2	Atom 3		Atom 1	Atom 2	Atom 3	
C(2)	-C(1)	-C(10)	116.0 (2)	C(14)	-C(13)	-C(18)	108.7 (2)
C(3)	-C(2)	-C(1)	111.2 (3)	C(14)	-C(13)	-C(26)	111.6 (3)
C(4)	-C(3)	-C(2)	113.4 (3)	C(12)	-C(13)	-C(18)	111.0 (3)
C(4)	-C(3)	-O(2)	107.7 (3)	C(12)	-C(13)	-C(26)	107.2 (3)
C(2)	-C(3)	-O(2)	108.3 (3)	C(18)	-C(13)	-C(26)	110.4 (3)
C(5)	-C(4)	-C(3)	108.3 (3)	C(15)	-C(14)	-C(8)	108.5 (3)
C(5)	-C(4)	-C(23)	109.2 (3)	C(15)	-C(14)	-C(13)	109.0 (3)
C(5)	-C(4)	-C(24)	109.8 (3)	C(15)	-C(14)	-C(27)	107.4 (3)
C(3)	-C(4)	-C(23)	108.4 (3)	C(8)	-C(14)	-C(13)	109.8 (2)
C(3)	-C(4)	-C(24)	111.2 (3)	C(8)	-C(14)	-C(27)	110.3 (3)
C(23)	-C(4)	-C(24)	109.9 (3)	C(13)	-C(14)	-C(27)	111.7 (3)
C(6)	-C(5)	-C(4)	115.3 (3)	C(16)	-C(15)	-C(14)	116.4 (3)
C(6)	-C(5)	-C(10)	120.9 (3)	C(17)	-C(16)	-C(15)	117.2 (4)
C(6)	-C(5)	-O(1)	112.2 (3)	C(18)	-C(17)	-C(16)	113.1 (3)
C(4)	-C(5)	-C(10)	121.1 (3)	C(18)	-C(17)	-C(22)	109.1 (3)
C(4)	-C(5)	-O(1)	113.4 (3)	C(18)	-C(17)	-C(28)	112.1 (3)
C(10)	-C(5)	-O(1)	59.2 (2)	C(16)	-C(17)	-C(22)	107.2 (3)
C(7)	-C(6)	-C(5)	115.3 (3)	C(16)	-C(17)	-C(28)	107.8 (3)
C(8)	-C(7)	-C(6)	111.1 (3)	C(22)	-C(17)	-C(28)	107.2 (3)
C(9)	-C(8)	-C(7)	108.7 (3)	C(19)	-C(18)	-C(13)	112.0 (3)
C(9)	-C(8)	-C(14)	116.6 (2)	C(19)	-C(18)	-C(17)	111.8 (3)
C(7)	-C(8)	-C(14)	114.0 (3)	C(13)	-C(18)	-C(17)	113.8 (3)
C(10)	-C(9)	-C(8)	108.3 (2)	C(20)	-C(19)	-C(18)	116.8 (3)
C(10)	-C(9)	-C(11)	109.9 (2)	C(21)	-C(20)	-C(19)	109.5 (4)
C(10)	-C(9)	-C(25)	105.6 (2)	C(21)	-C(20)	-C(29)	110.2 (4)
C(8)	-C(9)	-C(11)	108.4 (2)	C(21)	-C(20)	-C(30)	109.4 (4)
C(8)	-C(9)	-C(25)	115.0 (3)	C(19)	-C(20)	-C(29)	110.4 (4)
C(11)	-C(9)	-C(25)	109.5 (3)	C(19)	-C(20)	-C(30)	107.8 (4)
O(1)	-C(10)	-C(1)	110.9 (2)	C(29)	-C(20)	-C(30)	109.5 (4)
O(1)	-C(10)	-C(5)	59.4 (2)	C(22)	-C(21)	-C(20)	113.1 (4)
O(1)	-C(10)	-C(9)	114.9 (2)	C(17)	-C(22)	-C(21)	112.2 (4)
C(1)	-C(10)	-C(5)	120.6 (3)	C(32)	-C(31)	-O(2)	110.9 (4)
C(1)	-C(10)	-C(9)	116.4 (2)	C(32)	-C(31)	-O(3)	124.9 (4)
C(5)	-C(10)	-C(9)	120.0 (3)	O(2)	-C(31)	-O(3)	124.2 (4)
C(12)	-C(11)	-C(9)	113.8 (3)	C(3)	-O(2)	-C(31)	118.2 (3)
C(13)	-C(12)	-C(11)	113.0 (3)	C(5)	-O(1)	-C(10)	61.4 (2)
C(14)	-C(13)	-C(12)	107.9 (2)				

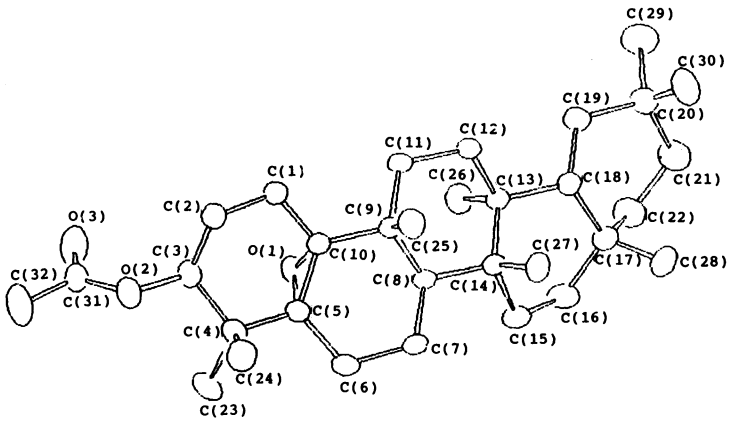
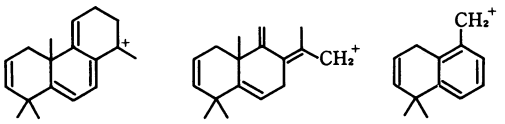


Fig. 1. Perspective view of 5α,10α-epoxyalnusan-3β-yl acetate (**6**).

mum above 210 nm, while the ^{1}H NMR spectrum revealed the presence of a doubly allylic methylene (δ 2.60, 2H; m) and an olefinic proton (δ 5.71, 1H; dd). The spectral data and mechanistic considerations lead to the structure, multiflora-5,8-dien-3β-yl acetate for the main product (**24**). The proposed structure was supported by the mass spectral measurement; the appearance of the fragment peaks at *m/z* 239 (**A**), *m/z* 227 (**B**), and *m/z* 171 (**C**) indicates the presence of the 5,8-diene structure.



A $C_{18}H_{23}^+$ (*m/z* 239.1798) **B** $C_{17}H_{23}^+$ (*m/z* 227.1778) **C** $C_{13}H_{15}^+$ (*m/z* 171.1207)

The seven minor products obtained by the BF_3·OEt_2-catalyzed backbone rearrangement of **6** could not be identified, because of difficulty of the separation and a paucity of the material.

The diene (**24**) was treated with selenium dioxide[12] in boiling aqueous benzene to give a dehydrogenation product (**25**), the molecular formula, $C_{32}H_{48}O_2$, of which was given by the high-resolution mass spectrum. Since the ^{1}H NMR and UV spectra indicate the presence of a $\Delta^{5,7,9(11)}$-triene moiety, the stucture of the dehydrogenation product (**25**) is formulated as multiflora-5,7,9(11)-trien-3β-yl acetate.

The backbone rearrangement of 5α,10α-epoxyalnusan-3β-yl acetate (**6**) was shown to yield multiflora-5,8-dien-3β-yl acetate (**24**) as the main rearranged product, no further rearranged product being obtained much enough to be characterized. Although it is not clear the reason why further migration did not occur efficiently, the following account could be proposed. On attack of BF_3·OEt_2, the 5α,10α-epoxide ring would be cleaved to yield a carbonium ion on C-10 and a BF_3-coordinated oxygen-function at C-5α. A methyl group at C-9β would migrate to C-10 and then a migration of $C_{8\alpha}$–H to C-9α would follow immediately to afford a carbonium ion on C-8. If the BF_3-coordinated group is absent, it is expected to take place the further backbone rearrangement up to the C and D rings. However, since the BF_3-coordinated group at C-5α and the $C_{9\alpha}$–H are located in a 1,3-diaxial relationship, the neighboring group participation could assist the abstraction of the $C_{9\alpha}$–H, while the competitive migration of C_{14}–Me would be impeded, resulting in the interruption of the further backbone rearrangement.

The diene (**24**) in ethyl acetate was hydrogenated in the presence of 5% palladium on carbon for 3 d to give a hydrogenation product in 97% yield, which was shown to be a mixture of **26** and **27** in a ratio of 2:3 by GC examination. The mixture was subjected to separation by repeating column chromatography on silica gel to afford isomutiflorenyl acetate (**26**) and its 5β-*H* isomer (**27**). The spectral data of the former (**26**) were identical with those of literatures[4] and two compounds (**26** and **27**) exhibited nearly the same mass spectra characteristic of multiflor-8-ene skeleton.[13] Since the diene molecule (**24**) bends towards the α-side so much that the adsorption onto the surface of the catalyst was impeded, the hydrogenation from the α-side was hindered. On the other hand, the hydrogenation from the β-side was also hindered by the presence of 4β- and 10β-methyl groups. The fact that the hydrogenation had required a long reaction time could be explained by these two effects, which were estimated to be almost the same from the product ratio.

Isomultiflorenyl acetate (**26**) and its 5β-*H* isomer (**27**) were hydrolyzed with alkali to give isomultiflorenol (**1**)[6,14,15] and 5β-isomultiflorenol (**28**), respectively.

Thus the conversion of dendropanoxide (**5**) into isomultiflorenol (**1**) was achieved in 18% overall yield (6 steps) through thermodynamically favorable pathways,[16] which formally constitutes the total synthesis of isomultiflorenol (**1**).[17]

When the acetate mixture (**26** and **27**), obtained by the hydrogenation of the diene (**24**), was treated with 5% potassium hydroxide in methanol–tetrahydrofuran (5:1) at room temperature, the acetate (**26**) was easily hydrolyzed and afforded isomultiflorenol (**1**) within a half day, while most of the acetate (**27**) still remained intact; it required additional 4 d for completion of the hydrolysis of **27**.

Isomultiflorenol (**1**) and the 5β-*H* isomer (**28**) were subjected to Collins oxidation to give isomultiflorenone (**29**) and the 5β-*H* ketone (**30**), respectively. Isomultiflorenone (**29**)[15,18] exhibits IR absorption band at 1710 cm^{-1} and the positive Cotton effect. 5β-Isomultiflorenone (**30**) shows IR absorption band at 1715 cm^{-1}, intense fragment peaks at *m/z* 257 and *m/z* 245 chracteristic of the multiflor-8-ene skeleton,[13] and the negative Cotton effect.

Experimental[19]

Epoxidation of Alnus-5(10)-en-3β-yl Acetate (4). Alnus-5(10)-en-3β-ol (**7**), prepared from dendropanoxide (**5**), was acetylated with acetic anhydride in pyridine to give alnus-5(10)-en-3β-yl acetate (**4**), mp 289—293 °C. The acetate (**4**; 224 mg) was dissolved in chloroform (20 ml) and treated with MCPBA (208 mg) and disodium hydrogenphosphate dodecahydrate (Na_2HPO_4·$12H_2O$; *ca.* 5 mg) at 0 °C for 7 h. The usual work-up gave a residue (224 mg; 97% yield), which was purified by silica-gel (30 g) column chromatography. Elution with benzene afforded 5α,10α-epoxyalnusan-3β-yl acetate (**6**), mp 272—273 °C (from $CHCl_3$–CH_3OH); IR (KBr) 1730, 1250, 1025, 990, and 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.97 (3H, s), 0.99 (6H, s), 1.02 (6H, s), 1.03 (6H, s), 1.15 (3H, s), 2.00 (3H, s), and 4.77 (1H, dd, J=10

and 4 Hz); MS *m/z* (%) 484 (M^+; 5), 466 (14), 406 (100), 391 (42), 227 (22), 205 (32), and 202 (46); Found: *m/z* 484.3867. Calcd for $C_{32}H_{52}O_3$: M, 484.3914.

Epoxidation of Alnus-5(10)-en-3β-ol (7). Alnus-5(10)-en-3β-ol (**7**; 118 mg) in chloroform (10 ml) was treated with MCPBA (122 mg) and $Na_2HPO_4 \cdot 12H_2O$ (*ca.* 5 mg) at 0 °C for 4 h. The usual work-up afforded 5α,10α-epoxyalnusan-3β-ol (**9**; quantitative yield), mp 247—248 °C (from acetone) (decomp); IR (KBr) 3450, 1690, 1050, 1020, 1000, and 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (6H, s), 1.00 (6H, s), 1.01 (3H, s), 1.03 (3H, s), 1.07 (3H, s), 1.15 (3H, s), and 3.58 (1H, dd, *J*=10 and 5 Hz); MS *m/z* (%) 442 (M^+; 3), 427 (7), 424 (47), 409 (14), 406 (9), 391 (36), 245 (25), 206 (100), 201 (32), 109 (50), and 95 (54).

5α,10α-Epoxyalnusan-3β-ol (**9**; 37 mg) was treated with acetic anhydride (1 ml) and pyridine (4 ml) at room temperature for 14 h to give **6** in 95% yield.

Epoxidation of Alnus-5(10)-en-3β-yl Benzoate (8). Alnus-5(10)-en-3β-ol (**7**; 33 mg) was benzoylated with benzoyl chloride (1 ml) and pyridine (5 ml) at room temperature for 1 h to give the benzoate (**8**; 36 mg), mp 273—274 °C (from $CHCl_3$–acetone); IR (KBr) 1715, 1280, 1115, 705, and 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (6H, s), 1.04 (12H, s), 1.14 and 1.18 (each 3H, s), 4.94 (1H, dd, *J*=10 and 4 Hz), and 7.35—8.14 (5H); MS *m/z* (%) 530 (M^+; 0.5), 515 (0.2), 408 (66), 393 (30), 365 (21), 205 (28), 203 (37), 190 (36), 189 (36), 187 (39), 175 (42), and 105 (100).

The benzoate (**8**; 33 mg) in chloroform (5 ml) was epoxidized with MCPBA (27 mg) and $Na_2HPO_4 \cdot 12H_2O$ (*ca.* 2 mg) at 0 °C for 3 h to afford 5α,10α-epoxyalnusan-3β-yl benzoate (**10**; 28 mg), mp 272—278 °C (from $CHCl_3$–CH_3OH) (decomp); IR (KBr) 1715, 1275, 1115, and 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95, 0.99, 1.02, 1.04, 1.06, 1.08 (each 3H, s), 1.19 (6H, s), 5.02 (1H, dd, *J*=11 and 4 Hz), and 7.37—8.13 (5H); MS *m/z* (%) 546 (M^+; 0.6), 528 (3), 406 (43), 391 (41), 274 (18), 259 (20), 205 (30), 201 (19), 187 (24), 185 (25), 171 (41), and 105 (100).

On treatment with lithium aluminium hydride, the epoxy benzoate (**10**; 24 mg) afforded 5α,10α-epoxyalnusan-3β-ol (**9**; 15 mg) identical with an authentic sample.

Epoxidation of Alnus-5(10)-en-3α-ol (11). Alnus-5(10)-en-3α-ol (**11**, 21 mg), mp 255—258 °C, was dissolved in chloroform (5 ml) and treated with MCPBA (22 mg) and $Na_2HPO_4 \cdot 12H_2O$ (*ca.* 2 mg) at 0 °C for 1.5 h. The usual work-up gave 5α,10α-epoxyalnusan-3α-ol (**13**; 20 mg), mp 272—276 °C (from C_6H_6–CH_3OH) (decomp); IR (Nujol) 3480 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (3H, s), 1.00 (9H, s), 1.02, 1.05 (each 3H, s), 1.17 (6H, s), 3.24 (1H, dt, *J*=11 and 3 Hz), and 3.52 (1H, d, *J*=11 Hz; disappeared on addition of D_2O); MS *m/z* (%) 442 (M^+; 0.8), 424 (79), 406 (17), 391 (46), 206 (100), 201 (48), 189 (38), 187 (35), 171 (35), 109 (65), and 95 (83).

5α,10α-Epoxyalnusan-3α-ol (**13**; 12 mg) was treated with acetic anhydride (3 ml) and pyridine (5 ml) at 120 °C for 4 h to give **14** in 53% yield.

Epoxidation of Alnus-5(10)-en-3α-yl Acetate (12). Alnus-5(10)-en-3α-yl acetate (**12**; 14 mg), mp 206—207 °C, in chloroform (3 ml) was epoxidized with MCPBA (21 mg) at 0 °C for 1.3 h to afford 5α,10α-epoxyalnusan-3α-yl acetate (**14**; 10 mg), mp 246—248 °C (from C_6H_6–CH_3OH); IR (KBr) 1740, 1255, 1030, 995, and 925 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (3H, s), 1.03 (18H, s), 1.15 (3H, s), 2.03 (3H, s), and 4.47 (1H, dd, *J*= 7 and 4 Hz); MS *m/z* (%) 484 (M^+; 0.3), 409 (6), 406 (8), 391 (59), 248 (19), 227 (20), 205 (38), 201 (43), 189 (75), 187 (53), 137 (95), 109 (82), and 95 (100).

Epoxidation of Alnus-5(10)-en-3α-yl Benzoate (15). Alnus-5(10)-en-3α-ol (**11**) was treated with benzoyl chloride and pyridine to afford the benzoate (**15**), mp 175—177 °C (from $CHCl_3$–CH_3OH); IR (KBr) 1720, 1280, 1120, 755, and 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96, 1.00, 1.01 (each 3H, s), 1.06, 1.09 (each 6H, s), 1.20 (3H, s), 4.96 (1H, dd, *J*=5 and 3 Hz), and 7.35—8.12 (5H); MS *m/z* (%) 530 (M^+; 4), 408 (93), 393 (36), 365 (33), 229 (21), 218 (24), 205 (39), 203 (37), 190 (39), 189 (45), 187 (40), 175 (39), and 105 (100).

Alnus-5(10)-en-3α-yl benzoate (**15**; 302 mg) in chloform (40 ml) was treated with MCPBA (246 mg) in the presence of $Na_2HPO_4 \cdot 12H_2O$ (*ca.* 10 mg) at 0 °C for 2 h. After the usual work-up, the reaction product was separated by column chromatography on silica gel (40 g) eluted with benzene to afford the major epoxide (**16**; 267 mg) and the minor epoxide (**17**; 35 mg). 5α,10α-Epoxyalnusan-3α-yl benzoate (**16**); mp 202—203 °C (from $CHCl_3$–CH_3OH); IR (KBr) 1720, 1275, 1115, and 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96, 1.00, 1.03, 1.06 (each 3H, s), 1.10 (6H, s), 1.15, 1.17 (each 3H, s), 4.72 (1H, dd, *J*=7 and 3 Hz), and 7.38—8.18 (5H); MS *m/z* (%) 546 (M^+; 2), 528 (19), 406 (32), 391 (64), 310 (16), 205 (26), 201 (26), 189 (37), 187 (31), 137 (40), and 105 (100). 5β,10β-Epoxyalnusan-3α-yl benzoate (**17**); mp 154—155 °C (from $CHCl_3$–CH_3OH); IR (film) 1720, 1275, 1115, 1025, 940, and 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97, 1.00, 1.02, 1.08 (each 3H, s), 1.09 (6H, s), 1.15, 1.20 (each 3H, s), 4.78 (1H, dd, *J*=5.5 and 3 Hz), and 7.33—8.18 (5H); MS *m/z* (%) 546 (M^+; 5), 424 (11), 406 (8), 391 (9), 288 (36), 274 (18), 273 (19), 219 (19), 218 (21), 205 (36), 189 (18), 185 (41), 137 (64), 109 (50), 105 (100), and 95 (61).

5α,10α-Epoxyalnusan-3α-yl benzoate (**16**; 22 mg) was treated with lithium aluminium hydride (5 mg) at room temperature for 30 min to give **13** in 68% yield.

5β,10β-Epoxyalnusan-3α-yl benzoate (**17**; 31 mg) was treated with a mixture of 5% potassium hydroxide (KOH) in methanol (6 ml) and tetrahydrofuran (THF) (2 ml) for 2 d to give 5β,10β-epoxyalnusan-3β-ol (**20**; 21 mg); mp 210—211 °C (from $CHCl_3$–CH_3OH); IR (KBr) 3580, 1070, and 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (6H, s), 1.02 (12H, s), 1.03, 1.17 (each 3H, s), and 3.41 (1H, dd, *J*=7 and 3 Hz); MS *m/z* (%) 442 (M^+; 10), 427 (12), 424 (70), 406 (10), 391 (12), 218 (24), 206 (100), 205 (40), 201 (50), 187 (25), 179 (31), 137 (41), 109 (54), and 95 (60).

5β,10β-Epoxyalnusan-3α-ol (**20**; 14 mg) was treated with acetic anhydride (1 ml) and pyridine (3 ml) at 100 °C for 4 h to give 5β,10β-epoxyalnusan-3α-yl acetate (**21**; 15 mg); mp 173—174 °C (from $CHCl_3$–CH_3OH); IR (KBr) 1730, 1250, 1050, 1020, and 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (6H, s), 0.98 (3H, s), 1.01 (9H, s), 1.05, 1.07, 2.03 (each 3H, s), and 4.57 (1H, dd, *J*=7 and 3 Hz); MS *m/z* (%) 484 (M^+; 41), 469 (16), 424 (19), 409 (18), 406 (17), 391 (12), 342 (11), 288 (98), 274 (62), 273 (60), 259 (21), 245 (28), 218 (79), 205 (91), 137 (100), 109 (59), and 95 (56).

Sharpless Epoxidation of Alnus-5(10)-en-3α-ol (11) and -3β-ol (7). Alnus-5(10)-en-3α-ol (**11**; 35 mg) was dissolved in benzene (7 ml) and treated with the benzene solution of *t*-butyl hydroperoxide (80 μl; 2.35 mmol/ml)[10a] and $VO(acac)_2$ (*ca.* 1 mg) at room temperature in nitrogen atmosphere for 4 h. The usual work-up afforded 5α,10α-epoxyalnusan-3α-ol (**13**; 32 mg), which was identical with that obtained by the MCPBA-epoxidation of **11**.

Alnus-5(10)-en-3β-ol (**7**; 47 mg) was treated with the ben-

zene solution of *t*-butyl hydroperoxide (100 μl) and VO (acac)$_2$ (*ca.* 1 mg) under the same conditions for 7 h to give 5β,10β-epoxyalnusan-3β-ol (**18**; 34 mg); mp 199—200 °C (from acetone); IR (film) 3380, 1055, 1030, 995, and 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.97 (6H, s), 1.03 (3H, s), 1.06 (9H, s), 1.10, 1.18 (each 3H, s), 2.71 (1H, br; disappeared on addition of D_2O), and 3.17 (1H, br; changed into a triplet (*J*=5 Hz) on addition of D_2O); MS *m/z* (%) 442 (M^+; 2), 424 (91), 409 (18), 406 (30), 391 (100), 227 (49), 206 (87), 205 (47), 201 (55), 189 (76), 187 (62), 137 (65), 109 (84), and 95 (95); high resolution MS *m/z* 442.3797. Calcd for $C_{30}H_{50}O_2$: M, 442.3809.

5β,10β-Epoxyalnusan-3β-ol (**18**; 30 mg) was treated with acetic anhydride (1 ml) and pyridine (2 ml) at room temperature for 40 h to give 5β,10β-epoxyalnusan-3β-yl acetate (**22**; 25 mg); mp 258.5—259.5 °C (from $CHCl_3$–CH_3OH); IR (KBr) 1735, 1250, and 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.96 (6H, s), 1.01 (9H, s), 1.04 (6H, s), 1.17 (3H, s), 2.03 (3H, s), and 4.36 (1H, dd, *J*=11 and 4 Hz); MS *m/z* (%) 484 (M^+; 12), 469 (8), 466 (28), 451 (6), 424 (22), 409 (12), 406 (100), 391 (51), 342 (33), 288 (20), 274 (40), 259 (34), 218 (43), 205 (73), 137 (72), 109 (70), and 95 (83).

5β,10β-Epoxyalnusan-3β-ol (**18**; 31 mg) was benzoylated with benzoyl chloride (0.1 ml) and pyridine (2 ml) at room temperature for 1.5 h to give 5β,10β-epoxyalnusan-3β-yl benzoate (**23**; 23 mg); mp 245—246 °C (from $CHCl_3$–CH_3OH); IR (KBr) 1720, 1275, 1115, 1025, and 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.97, 1.03, 1.07, 1.20 (each 6H, s), 4.62 (1H, dd, *J*=10 and 5 Hz), and 7.38—8.12 (5H); MS *m/z* (%) 546 (M^+; 12), 424 (49), 409 (22), 406 (34), 391 (16), 342 (18), 288 (26), 274 (20), 273 (22), 249 (17), 218 (35), 205 (53), 137 (85), 105 (100), and 95 (52).

Oxidation of 5α,10α-Epoxyalnusan-3β-ol (9) and 5α,10α-Epoxyalnusan-3α-ol (13). 5α,10α-Epoxyalnusan-3β-ol (**9**; 56 mg) and -3α-ol (**13**; 22 mg) were oxidized with Collins reagent to give the same product, 5α,10α-epoxyalnusan-3-one (**19**; 43 mg and 11 mg, respectively), mp 261—263 °C (from $CHCl_3$–CH_3OH) (decomp); IR (KBr) 1710 and 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.94, 0.99 (each 3H, s), 1.04 (6H, s), 1.11, 1.13, 1.15, 1.17 (each 3H, s), and 2.24 (2H, t, *J*=6 Hz); MS *m/z* (%) 440 (M^+; 12), 425 (11), 422 (19), 407 (9), 205 (97), 204 (87), 177 (53), 137 (44), 123 (57), 109 (81), and 95 (100).

Backbone Rearrangement of 5α,10α-Epoxyalnusan-3β-yl Acetate (6). 5α,10α-Epoxyalnusan-3β-yl acetate (**6**; 121 mg) in benzene (30 ml) was treated with $BF_3 \cdot OEt_2$ (38 μl; 1.1 equiv) at room temperature in nitrogen atmosphere for 30 min. The reaction product, after addition of a saturated sodium hydrogencarbonate solution, was worked up as usual to give a residue (117 mg). The residue showed eight peaks at 12.8, 16.5, 18.9 (a main peak; a ratio of the product was estimated at *ca.* 80% from the peak hight), 21.1, 22.1, 23.9, 25.7, and 27.9 min on HPLC (column: μPORASIL, solvent system; 1% ether–hexane, 1 ml/min). The residue was chromatographed on alumina (Alumina Woelm N, Akt I. 35 g; impregnated with 15% silver nitrate). Elution with 5—10% ethyl acetate–hexane afforded a mixture (*ca.* 24 mg) of the minor products and the product, multiflora-5,8-dien-3β-yl acetate (**24**; 81.4 mg). The latter was purified by column chromatography on silica gel eluted with hexane–benzene to give pure **24**, mp 190—193 °C (from C_6H_6–CH_3OH); IR (KBr) 1735, 1250, 1035, 1020, and 990 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.98 (6H, s), 1.01 (3H, s), 1.10 (6H, s), 1.12, 1.14, 1.18, 2.04 (each 3H, s), 2.60 (2H, m), 4.50 (1H, dd, *J*=8 and 6 Hz), and 5.71 (1H, dd, *J*=5 and 3 Hz); ^{13}C NMR ($CDCl_3$) δ=19.2, 21.1, 21.3, 24.1, 25.1, 25.2, 25.2, 25.8, 27.1, 27.6, 28.3, 30.9, 31.1, 31.7, 33.1, 33.8, 34.2, 34.5, 34.5, 36.8, 36.8, 37.3, 38.4, 40.4, 40.7, 44.2, 79.1, 120.2, 131.1, 134.0, 146.4, and 170.7; MS *m/z* (%) 466 (M^+; 5), 406 (15), 391 (100), 239 (13), 227 (28), 187 (18), 185 (20), and 171 (43); high resolution MS *m/z* 466.3791 (Calcd for $C_{32}H_{50}O_2$: M, 466.3809), *m/z* 239.1798 (Calcd for $C_{18}H_{23}$: 239.1798), *m/z* 227.1778 (Calcd for $C_{17}H_{23}$: 227.1798), and *m/z* 171.1207 (Calcd for $C_{13}H_{15}$: 171.1174).

Dehydrogenation of Multiflora-5,8-dien-3β-yl Acetate (24). The diene (**24**; 39 mg) was heated with selenium dioxide in a mixture of benzene (5 ml) and water (5 drops) under reflux for 38 h to give multiflora-5,7,9(11)-trien-3β-yl acetate (**25**; 22 mg), mp 211—214 °C (from $CHCl_3$–CH_3OH); IR (KBr) 1740, 1250, 1035, 1005, 980, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.84, 0.96, 0.99, 1.02, 1.06, 1.09 (each 3H, s), 1.21 (6H, s), 2.07 (3H, s), 4.57 (1H, dd, *J*=6 and 5 Hz), 5.38 (1H, m), 5.57 (1H, d, *J*=6 Hz), and 5.89 (1H, d, *J*=6 Hz); UV λ(C_2H_5OH) 307 (ε 11600) and 317 nm (12200); MS *m/z* (%) 464 (M^+; 7), 404 (100), 389 (21), 251 (26), 237 (26), and 225 (80); high resolution MS *m/z* 464.3649 (Calcd for $C_{32}H_{48}O_2$: M, 464.3654), *m/z* 237.1645 (Calcd for $C_{18}H_{21}$: 237.1643), and *m/z* 225.1661 (Calcd for $C_{17}H_{21}$; 225.1644).

Hydrogenation of Multiflora-5,8-dien-3β-yl Acetate (24). A solution of multiflora-5,8-dien-3β-yl acetate (**24**; 103 mg) in ethyl acetate (70 ml) was hydrogenated in the presence of 5% palladium on carbon (470 mg) for 3 d to give hydrogenated products (101 mg), which showed two peaks at 16.3 and 21.4 min (peak hight ratio 3:2) on GC examination (column: Dexsil 300 GC, 2%, 1.5 m) and two peaks at 20.2 and 22.2 min (peak hight ratio 2:3) on HPLC examination. (column: μPORASIL, solvent system: 0.8% ether–hexane, 1 ml/min). The mixture was separated by repeating column chromatography on silica gel to give isomultiflorenyl acetate (**26**; 40 mg) and 5β-isomultiflorenyl acetate (**27**; 60 mg). Isomultiflorenyl acetate (**26**); mp 223—225 °C (from CH_2Cl_2–CH_3OH); IR (KBr) 1735, 1455, 1380, 1255, 1025, 1005, and 990 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88, 0.96, 0.98 (each 6H, s), 1.06, 1.07, (each 3H, s), 2.03 (3H, s), and 4.48 (1H, dd, *J*=11 and 5 Hz); MS *m/z* (%) 468 (M^+; 58), 453 (15), 408 (21), 393 (23), 301 (28), 289 (17), 241 (26), 229 (27), 218 (64), 205 (100), 203 (47), and 189 (23). 5β-Isomultiflorenyl acetate (**27**); mp 151—152 °C (from CH_2Cl_2–CH_3OH); IR (film) 1730, 1245, and 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.94 (3H, s), 0.97, 1.03 (each 6H, s), 1.06 (3H, s), 1.08 (6H, s), 2.04 (3H, s), and 4.54 (1H, t, *J*=3 Hz); MS *m/z* (%) 468 (M^+; 74), 453 (58), 408 (21), 393 (62), 301 (57), 289 (29), 241 (100), 229 (93), 205 (94), 203 (49), and 189 (58); high resolution MS *m/z* 468.3960. Calcd for $C_{32}H_{52}O_2$: M, 468.3965.

Hydrolysis of Isomultiflorenyl Acetate (26) and Its 5β-H Isomer (27). Isomultiflorenyl acetate (**26**; 15 mg) was treated with a mixture of 5% KOH in methanol (50 ml) and THF (10 ml) at room temperature in nitrogen atmosphere for 1 d. The usual work-up gave isomultiflorenol (**1**; 13 mg); mp 182—183 °C (from $CHCl_3$–CH_3OH); IR (Nujol) 3350 and 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.80 (3H, s), 0.97 (9H, s), 0.99, 1.00, 1.06, 1.07 (each 3H, s), and 3.23 (1H, dd, *J*=11 and 5 Hz); MS *m/z* (%) 426 (M^+; 100), 411 (29), 408 (31), 393 (43), 259 (83), 247 (55), 241 (56), 229 (65), 218 (77), 205 (98), 204 (50), 191 (40), and 189 (44); high resolution MS *m/z* 426.3863. Calcd for $C_{30}H_{50}O$: M, 426.3862.

5β-Isomultiflorenyl acetate (**27**; 25 mg) was treated with

5% KOH in methanol–THF (5:1, 40 ml) under the same conditions as above for 4 d to afford 5β-isomultiflorenol (**28**; 20 mg); mp 159—159.5 °C (from ether–CH_3OH); IR (film) 3430, 1060, 950, and 935 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.98 (6H, s), 1.04 (12H, s), 1.09 (6H, s), and 3.33 (1H, t-like, J=3 Hz); MS m/z (%) 426 (M^+; 32), 411 (92), 408 (19), 393 (63), 259 (87), 247 (38), 241 (100), 229 (85), 205 (65), 203 (37), 189 (87), 109 (90), and 95 (88); high resolution MS m/z 426.3907 (Calcd for $C_{30}H_{50}O$: M, 426.3862), m/z 259.2060 (Calcd for $C_{18}H_{27}O$: 259.2060), m/z 247.2065 (Calcd for $C_{17}H_{27}O$: 247.2062), m/z 241.1944 (Calcd for $C_{18}H_{25}$; 241.1955), and m/z 229.1967 (Calcd for $C_{17}H_{25}$: 229.1956).

Oxidation of Isomultiflorenol (1) and 5β-Isomultiflorenol (28). Isomultiflorenol (**1**; 17 mg) in dichloromethane (5 ml) was oxidized with Collins reagent (4 ml; 17 eq) at room temperature for 16 min to give isomultiflorenone (**29**; 16 mg); mp 189—193 °C (from $CHCl_3$–CH_3OH); IR (KBr) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (6H, s), 0.99 (3H, s), 1.06 (6H, s), 1.10 (9H, s), and 2.40—2.62 (2H, m); MS m/z (%) 424 (M^+; 16), 409 (7), 257 (48), 245 (39), 205 (100), 109 (38), and 95 (54). CD (c 0.016, $CHCl_3$, Amb. temp.) $[\theta]_{291}$ +1580 and $[\theta]_{323}$ −110.

5β-Isomutiflorenol (**28**; 18 mg) was oxidized with Collins reagent (4 ml; 16 eq) under the same conditions as above to give 5β-isomultiflorenone (**30**; 17 mg), mp 143—144 °C (from ether–CH_3OH); IR (KBr) 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (6H, s), 1.02 (3H, s), 1.10 (6H, s), 1.11, 1.14, 1.16 (each 3H, s) and 2.16—2.40 (2H, m); MS m/z (%) 424 (M^+; 16), 409 (11), 257 (73), 245 (60), 205 (100), 109 (39), and 95 (56); CD (c 0.016, $CHCl_3$, Amb. temp) $[\theta]_{314}$ −750, $[\theta]_{305}$ −880, and $[\theta]_{273}$ +120.

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