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Boron Trifluoride Etherate-catalyzed Backbone Rearrangement of 13*β*,18*β*-Epoxybaccharan-3*β*-yl Acetate. A Sequential Migration of Two Methyl Groups and a Hydride in Biogenetic Direction[1)]

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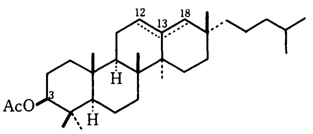
13*β*,18*β*-Epoxybaccharan-3*β*-yl acetate was treated with boron trifluoride etherate in acetic anhydride to afford a complex mixture, in which a formation of backbone rearrangement products, *D*:*C*-friedobacchar-9(11)-en- and -7-en-3*β*-yl acetates together with 3*β*-acetoxy-*D*-friedo-13,18-secobacchar-13-en-18-ylidene diacetate was observed. The *D*:*C*-friedobacchar-9(11)-ene derivative is the first example of the backbone rearrangement product formed by a sequential migration of two methyl groups and a hydride towards the biogenetic direction in baccharene-shionene series.

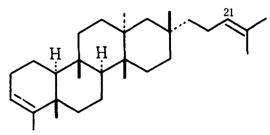
In biogenetic processes of triterpenes, some proceed enzymatically in direction to produce thermodynamically unstable products.[2)] A biogenesis of friedelin from oleanene-type precursor is known as a typical example of such energetically unfavorable processes.

Owing to the greater thermodynamic stability of the oleanene skeleton, most of the chemically-induced backbone rearrangement in oleanene-friedelene series proceed in the opposite direction from the biogenesis. On treatment with acid, for example, fridel-3-ene affords an equilibrium mixture of olean-13(18)-ene and 18*α*-olean-12-ene.[2)] Besides oleanene-friedelene series, the reactions of ursene-, lupene-, and baccharene-type triterpenes with acid do not give friedo-type triterpenes which would be produced by the biogenetic-like backbone rearrangement. However, it is possible to bring about the energetically unfavorable rearrangement in the biogenetic direction by combination with a free-energy releasing reaction which provides the thermodynamic driving force. Corey *et al.*[3)] reported backbone rearrangements of oleanene derivatives in the biogenetic direction under oxidative conditions. Paryzek[4)] and Baddeley *et al.*[5)] described the acid-catalyzed reaction of 9(11)-epoxylanostane derivatives in order to effect $C_{10}\rightarrow C_9$ methyl rearrangement. In these reactions, however, only one methyl group shifted towards biogenetic-like direction. Occurrence of a sequential multigroup rearrangement has never been observed so far.

The thermodynamic stability of baccharane skeleton was demonstrated by the following evidence. Treatment of bacchar-13(18)-en-3*β*-yl acetate (**1**)[6)] with hydrogen chloride in chloroform was found to yield a 1:1 mixture of bacchar-12-en-3*β*-yl acetate (**2**) and the starting material (**1**) by GLC examination; no skeletal rearrangement occurred. On the other hand, it has been shown that shiona-3,21-diene (**3**) is rearranged on treatment with boron trifluoride etherate ($BF_3 \cdot OEt_2$) to give *D*:*C*-friedobacchara-9(11),21-diene (**4**) and bacchara-12,21-diene (**5**),[7)] Therefore the baccharane skeleton was proved to be thermodynamically the most stable skeleton in the baccharene-shionene series.



1 13(18)-ene
2 12-ene



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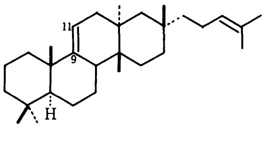

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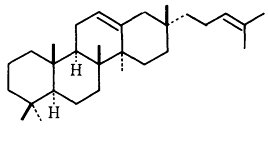

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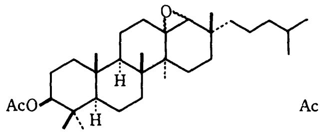
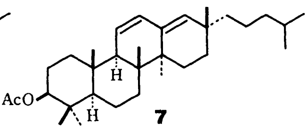
Paryzek[4b)] recommended the use of acetic anhydride as a solvent in a $BF_3 \cdot OEt_2$-catalyzed backbone rearrangement, because BF_3–Ac_2O system is expected to be a useful reagent in which efficient skeletal rearrangements induced by an epoxide cleavage may proceed. Therefore, backbone rearrangement of 13*β*,18*β*-epoxybaccharan-3*β*-yl acetate (**6b**) in acetic anhydride was first examined.

13*β*,18*β*-Epoxybaccharan-3*β*-yl acetate (**6b**) was prepared by epoxidation of bacchar-13(18)-en-3*β*-yl acetate (**1**)[6,8)] with *m*-chloroperbenzoic acid (MCPBA). The epoxidation product was a mixture of *α*- and *β*-epoxides (**6a** and **6b**) in a ratio of 1:9, which was separated by silica-gel column chromatography. The configuration of the epoxy ring was easily assignable from the ^{1}H NMR spectra.

13β,18β-Epoxybaccharan-3β-yl acetate (**6b**) was treated with $BF_3\cdot OEt_2$ in acetic anhydride at 0 °C. The reaction product was separated by silica-gel column chromatography into three fractions, **A**, **B**, and **C**.



6a 13α,18α-epoxide
6b 13β,18β-epoxide



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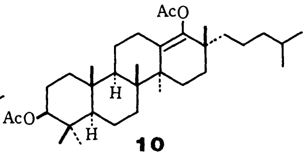

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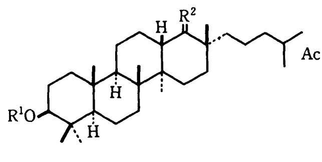
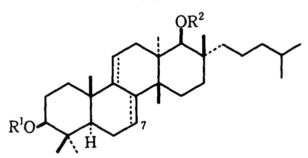
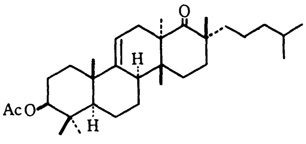


8 R^1= H, R^2= α-OH,β-H
9 R^1= Ac, R^2= O



11 9(11)-ene; R^1= R^2= H
12 7-ene; R^1= R^2= H
14 9(11)-ene; R^1= R^2=Ac
15 7-ene; R^1= R^2= Ac
23 9(11)-ene; R^1= Ac, R^2= H
24 7-ene; R^1= Ac, R^2= H



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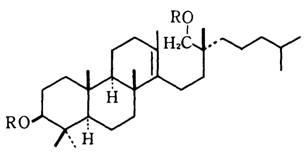
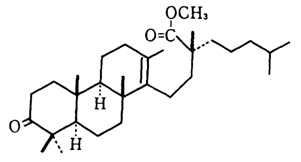


16 R= H
17 R= Ac
20 R= $OCOC_6H_5$



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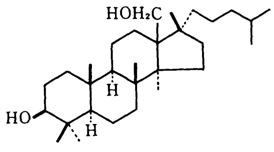

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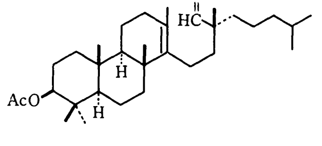


21 R= O
22 R= $\langle^{OAc}_{OAc}$

The fraction **A** was found to be bacchara-11,13(18)-dien-3β-yl acetate (**7**)[6] from the spectral data. The fraction **B** and **C** were shown to be mixtures by ^{1}H NMR spectral measurement, but each could not be separated by silica-gel column chromatography. The fraction **B** gave complicated signals appearing at δ 2.03, 2.07 (each *ca.* 3H, s), 4.45 (1H, dd), 4.90 and 4.92 (total *ca.* 0.7H, each s), and *ca.* 5.3 (*ca.* 0.5H, m). The fraction **C** showed complex signals appearing at δ 2.04, 2.06, 2.09, and 2.20 (each s), 3.35 (0.3—0.4H, m), *ca.* 4.45 (1H, m), 4.87 (0.3—0.4H, s), *ca.* 5.3 (0.1—0.2H, m), 6.69 and 6.71 (total *ca.* 0.4H, each s). On treatment with lithium aluminium hydride, the fraction **B** could be separated into three compounds, **B**$_1$, **B**$_2$, and **B**$_3$ and the fraction **C** three compounds, **C**$_1$, **C**$_2$, and **C**$_3$ by silica-gel column chromatography, respectively.

The compound **B**$_1$ was identical with an authentic baccharane-3β,18α-diol (**8**).[8] Therefore the initial rearranged product is deduced to be bacchar-13(18)-ene-3β,18-diyl diacetate (**10**), which was formed directly by abstraction of the hydrogen or *via* 18-oxobaccharan-3β-yl acetate (**9**)[9] followed by acetylation under the reaction conditions (Scheme 1 [**A**]-*b*). The formation of **9** was supported by the rearrangement of **6b** in benzene (*vide infra*).

The compound **B**$_2$, $C_{30}H_{52}O_2$, was a diol with a trisubstituted double bond, which was proved from the presence of a multiplet signal due to an olefinic proton at δ 5.38 in the ^{1}H NMR spectrum and characteristic fragment ion peaks at m/z 259 and m/z 247 in the mass spectrum. Comparison with olefinic signals of friedo-type triterpenes (see Table 1) revealed that the olefinic proton observed at δ 5.38 is corresponding to that of either 7-ene, 9(11)-ene, or 14-ene. A formation of the fragment ions at m/z 259 and m/z 247 is indicative of the presence of either 7-ene, 8-ene, or 9(11)-ene.[13] From these observations, the compound **B**$_2$ was inferred to be either *D*:*C*-friedobacchar-9(11)-ene-3β,18β-diol (**11**) or a 7-ene isomer (**12**). On acetylation followed by oxidation, the compound **B**$_2$ afforded a keto acetate (**13**), which showed a multiplet signal due to the olefinic proton at δ 5.38 in the ^{1}H NMR spectrum and fragment ion peaks at m/z 343 and m/z 344 in the mass spectrum. However, since further information concerning the exact position of the double bond could not be obtained from the spectral inspection for compound **B**$_2$ and its derivative (**13**), X-ray single crystal analysis was carried out for the keto acetate (**13**). The crystals of **13** belong to a monoclinic, space group $P2_1$, and the lattice parameters are a=17.273(9), b=11.981(5), and c=7.323(3) Å, β=99.13(3)°, and D_c=1.08 g·cm^{-3} with two molecules in a unit cell. Intensity data were measured on a Philips PW1100 automatic four-circle diffractometer using monochromated Cu *K*α radiation. A total of 2349 non-zero, independent reflections with $3° \leq \theta \leq 78°$ were obtained by 2θ—θ scanning mode. The structure was solved by the direct method using MULTAN 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 non-hydrogen atoms and the isotropic ones for the hydrogen atoms. The final atomic coordinates are listed in Table 2 and bond lengths and bond angles are listed in Tables 3 and 4.[14] Figure 1 is a computer-generated perspective drawing of the molecule of the keto acetate (**13**).

Thus the structure of the keto acetate was determined to be 18-oxo-*D*:*C*-friedobacchar-9(11)-en-3β-yl aceteate (**13**) and therefore the compound $\mathbf{B}_2$ is formulated as *D*:*C*-friedobacchar-9(11)ene-3β,18β-diol (**11**). This conclusion implies that the reaction product obtained by the backbone rearrangement of **6b** was *D*:*C*-friedobacchar-9(11)-ene-3β,18β-diyl diacetate (**14**).

The compound $\mathbf{B}_3$, $C_{30}H_{52}O_2$, was shown to be a double-bond isomer of $\mathbf{B}_2$ from the spectral data; it showed a multiplet signal at δ 5.35 in the ^{1}H NMR spectrum and fragment ion peaks at m/z 259 and m/z 247 in the mass spectrum. These spectral data lead to the conclusion that the compound $\mathbf{B}_3$ is formulated as *D*:*C*-friedobacchar-7-ene-3β,18β-diol (**12**) and therefore the rearranged product is *D*:*C*-friedobacchar-7-ene-3β,18β-diyl diacetate (**15**).

The compound $\mathbf{C}_1$ (**16**) showed the molecular formula, $C_{30}H_{54}O_2$ by the high-resolution mass spectrum and the ^{1}H NMR spectrum revealed the presence of two hydroxyl groups; one is secondary (δ 3.17, 1H, dd) and the other primary (δ 3.36, 2H, s). Since no signal due to unsaturation was observed in the ^{1}H NMR spectrum, the compound $\mathbf{C}_1$ was inferred to be either a tetracyclic saturated diol or a tricyclic diol with a tetrasubstituted double bond. On acetylation, the compound $\mathbf{C}_1$ afforded a diacetate (**17**), $C_{34}H_{58}O_4$, whose ^{1}H NMR spectrum showed the presence of an acetoxymethyl group (δ 3.82, 2H, s and δ 2.04, 3H, s) together with a secondary acetoxyl group (δ 4.46, 1H, dd and δ 2.04, 3H, s).

The presence of the hydroxymethyl group in the compound $\mathbf{C}_1$ was confirmed by the following chemical conversion. The compound $\mathbf{C}_1$ was oxidized with Jones reagent to give a keto carboxylic acid, which, without purification, was treated with diazomethane. The reaction product (**18**) showed the molecular ion at m/z 472 ($C_{31}H_{52}O_3$) and the presence of $COOCH_3$ group (δ 3.67, 3H,s; 1730 cm^{-1}) together with a carbonyl group (1705 cm^{-1}). From these evidence and mechanistic consideration, the structure of the compound $\mathbf{C}_1$ was inferred first to be 17(18$\rightarrow$13)*abeo*-baccharane-3β,18-diol (**19**). However, this structure assignment was found to be erroneous by X-ray diffraction analysis of the dibenzoate (**20**). Crystals of the dibenzoate (**20**) belong to orthorhombic, space group $P2_12_12_1$, and the lattice parameters are a=17.071(5), b=21.191(6), and c=10.870(3) Å and D_c=1.10 g·cm^{-3}. Four molecules are contained in the unit cell. Intensity data were measured by the same procedure as before and a total of 3173 non-zero, independent reflections with $3° \leq \theta \leq 78°$ were obtained by 2θ—θ scanning mode. The structure was solved and refined by the same procedure as before. The final R value was 0.066

TABLE 1. δ-VALUES OF OLEFINIC PROTONS OF FRIEDO-TYPE TRITERPENES

Compound	δ-Value	Lit,
Bacchar-5-en-3β-ol	5.62 m (6-H)	10)
Alnus-5-en-3β-ol	5.63 dd (6-H)	11)
D:*C*-Friedobacchar-7-en-3β-ol	5.39 q (7-H)	10)
D:*C*-Friedobacchara-7,21-diene	5.362 ddd (7-H)	7)
D:*C*-Friedobacchara-9(11),21-diene	5.301 ddd (11-H)	7)
Tarolupenyl acetate	5.325 ddd (15-H)	12)
Tarolupeol	5.333 ddd (15-H)	12)

TABLE 2. ATOMIC POSITIONAL PARAMETERS ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS ($\times 10^2$) FOR NON-HYDROGEN ATOMS OF KETO ACETATE (**13**) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	$B_{eq}$$^{a)}$
C(1)	590(3)	−943(0)	10815(6)	618(8)
C(2)	1456(3)	−952(5)	11475(6)	708(9)
C(3)	1807(2)	−2000(4)	10830(6)	600(8)
C(4)	1702(2)	−2108(4)	8733(6)	548(7)
C(5)	807(2)	−1994(4)	8021(5)	475(6)
C(6)	586(2)	−2167(4)	5912(6)	591(8)
C(7)	−255(3)	−2021(5)	5208(6)	721(10)
C(8)	−797(2)	−1951(4)	6597(5)	471(6)
C(9)	−512(2)	−1163(3)	8115(5)	466(6)
C(10)	371(2)	−978(4)	8660(5)	501(7)
C(11)	−1036(3)	−598(4)	9003(6)	589(8)
C(12)	−1898(3)	−687(4)	8528(6)	579(8)
C(13)	−2158(2)	−1773(4)	7477(5)	452(6)
C(14)	−1669(2)	−1897(4)	5858(5)	460(6)
C(15)	−1951(2)	−2945(4)	4736(6)	545(7)
C(16)	−2824(3)	−2873(5)	3921(7)	691(9)
C(17)	−3386(2)	−2619(4)	5287(6)	594(8)
C(18)	−3013(3)	−1755(4)	6740(6)	577(8)
C(19)	1984(3)	−3280(4)	8251(7)	658(9)
C(20)	2229(3)	−1253(5)	7917(7)	666(9)
C(21)	577(3)	150(4)	7813(7)	707(9)
C(22)	−1977(3)	−2732(4)	8911(6)	556(7)
C(23)	−1829(3)	−857(5)	4558(7)	674(9)
C(24)	−4145(3)	−2099(6)	4240(9)	897(12)
C(25)	−3579(3)	−3713(5)	6245(7)	695(9)
C(26)	−4076(3)	−3601(5)	7750(7)	731(10)
C(27)	−4259(3)	−4742(6)	8528(9)	878(12)
C(28)	−4741(4)	−4679(6)	10085(10)	1003(15)
C(29)	−5574(4)	−4292(7)	9445(13)	1167(19)
C(30)	−4728(4)	−5836(9)	11003(12)	1378(21)
C(31)	2840(3)	−2645(5)	13137(6)	639(8)
C(32)	3698(3)	−2659(7)	13763(9)	1056(14)
O(1)	2631(2)	−2066(3)	11580(4)	747(6)
O(2)	2369(2)	−3109(3)	13897(5)	803(7)
O(3)	−3442(2)	−1099(3)	7345(5)	819(7)

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

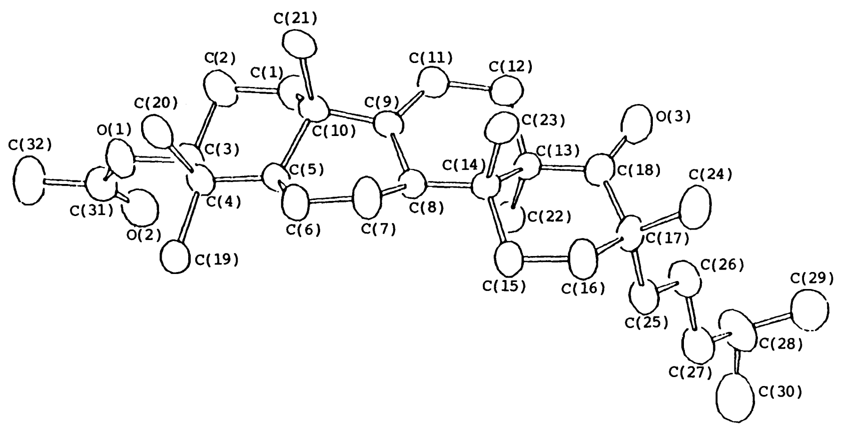


Fig. 1. Perspective view of 18-oxo-*D* : *C*-friedobacchar-9(11)-en-3β-yl acetate (**13**).

assuming the anisotropic temperature factors for non-hydrogen atoms and the isotropic ones for hydrogen atoms. The final atomic coordinates are listed in Table 5 and bond lengths and bond angles are listed in Tables 6 and 7.[14] Figure 2 is a computer-generated perspective drawing of the molecule of the dibenzoate (**20**), the structure being formulated as *D*-friedo-13,18-secobacchar-13-ene-3β, 18-diyl dibenzoate (**20**). Therefore, it is concluded that the initial rearranged product had been 3β-acetoxy-*D*-friedo-13,18-secobacchar-13-en-18-al (**21**), which was converted into its acylal (**22**) in the reaction conditions. This conclusion is supported by the presence of a singlet signal due to the acylal proton at δ 6.71 or δ 6.69 in the ^{1}H NMR spectrum of the fraction **C** (*loc. cit.*).

Table 3. Bond lengths (l/Å) of keto acetate (**13**) with estimated standard deviations in parentheses

Atom 1	Atom 2	Length	Atom 1	Atom 2	Length
C(1)	-C(2)	1.497(6)	C(13)	-C(14)	1.568(6)
C(1)	-C(10)	1.564(6)	C(13)	-C(18)	1.490(6)
C(2)	-C(3)	1.503(8)	C(13)	-C(22)	1.555(6)
C(3)	-C(4)	1.523(6)	C(14)	-C(15)	1.537(6)
C(3)	-O(1)	1.444(5)	C(14)	-C(23)	1.566(7)
C(4)	-C(5)	1.557(5)	C(15)	-C(16)	1.533(6)
C(4)	-C(19)	1.545(7)	C(16)	-C(17)	1.531(7)
C(4)	-C(20)	1.552(7)	C(17)	-C(18)	1.549(7)
C(5)	-C(6)	1.544(6)	C(17)	-C(24)	1.541(7)
C(5)	-C(10)	1.544(6)	C(17)	-C(25)	1.548(8)
C(6)	-C(7)	1.473(6)	C(18)	-O(3)	1.212(6)
C(7)	-C(8)	1.489(6)	C(25)	-C(26)	1.506(8)
C(8)	-C(9)	1.481(6)	C(26)	-C(27)	1.533(9)
C(8)	-C(14)	1.519(5)	C(27)	-C(28)	1.516(10)
C(9)	-C(10)	1.530(6)	C(28)	-C(29)	1.515(9)
C(9)	-C(11)	1.373(7)	C(28)	-C(30)	1.539(13)
C(10)	-C(21)	1.551(7)	C(31)	-C(32)	1.479(7)
C(11)	-C(12)	1.479(6)	C(31)	-O(1)	1.334(6)
C(12)	-C(13)	1.542(6)	C(31)	-O(2)	1.194(6)

The compound **C**$_3$ showed a molecular ion peak at m/z 488, which indicates an increment corresponding to a substituent, CH_3–CH(OH)–, compared with those of the olefinic diols **B**$_2$ (**11**) and **B**$_3$ (**12**). Therefore, the initial reaction product of the backbone rearrangement was deduced to possess an additional acetyl group. It is conceivable that the olefin, such as **14** or **15**, which had been produced by the rearrangement was subjected to acetylation, because the rearrangement conditions could bring about Friedel-Crafts reaction. However, further investigation on the structure of **C**$_3$ could not carried out because of a paucity of the material.

Since the compound **C**$_2$ was found to be a complex mixture of compounds derived from acetylated products by the ^{1}H NMR spectrum, this fraction was not further examined.

On treatment with $BF_3 \cdot OEt_2$ in acetic anhydride, 13β,18β-epoxybaccharan-3β-yl acetate (**6b**) has been shown to afford backbone rearrangement products, *D*:*C*-friedobacchar-9(11)-and-7-ene-3β,18β-diyl diacetates (**14** and **15**), 3β-acetoxy-*D*-friedo-13,18-secobacchar-13-en-18-ylidene diacetate (**22**), and many unidentified acetylated products. Formation of these reaction products can be reasonably explained by the reaction pathway depicted as in Scheme 1. The epoxide ring of **6b** was cleaved by the attack of $BF_3 \cdot Et_2O$ to give a carbonium ion [**A**] at C-13. Deprotonations, *a* and *b*, would produce **7** and **10**, respectively, while a consecutive 1,2-methyl migration (pathways *c* and *d*) would yield a carbonium ion [**C**] at C-8, which affords **15** and **14** by deprotonation and 1,2-hydride shift (*f*) followed by deprotonation, respectively. The formation of *D*:*C*-friedobacchar-9(11)-ene derivative (**14**) is thus demonstrated by a sequential shift of 14α-Me, 8β-Me, and 9α-H of the baccharane skeleton to 13α-Me, 14β-Me, and 8α-H, respectively. It is noteworthy that the formation of

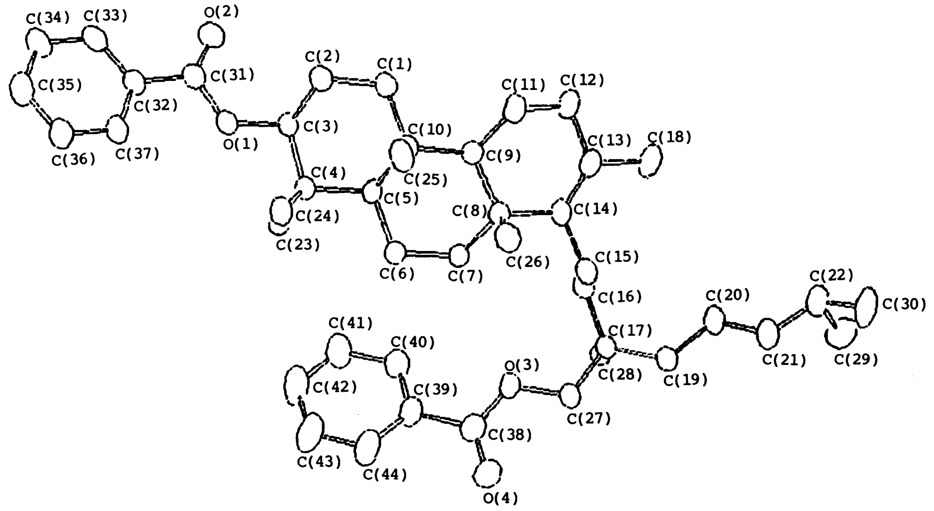


Fig. 2. Perspective view of *D*-friedo-13,18-secobacchar-13-ene-3β,18-diyl dibenzoate (**20**).

TABLE 4. BOND ANGLES (ϕ/°) OF KETO ACETATE (**13**) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(2)	-C(1)	-C(10)	113.3 (3)	C(14)	-C(13)	-C(22)	111.4 (3)
C(3)	-C(2)	-C(1)	109.7 (4)	C(12)	-C(13)	-C(18)	111.2 (3)
C(4)	-C(3)	-C(2)	113.5 (4)	C(12)	-C(13)	-C(22)	106.0 (3)
C(4)	-C(3)	-O(1)	109.3 (4)	C(18)	-C(13)	-C(22)	109.7 (3)
C(2)	-C(3)	-O(1)	110.4 (4)	C(15)	-C(14)	-C(8)	111.7 (3)
C(5)	-C(4)	-C(3)	106.5 (3)	C(15)	-C(14)	-C(13)	108.5 (3)
C(5)	-C(4)	-C(19)	109.5 (4)	C(15)	-C(14)	-C(23)	108.3 (3)
C(5)	-C(4)	-C(20)	115.2 (4)	C(8)	-C(14)	-C(13)	111.0 (3)
C(3)	-C(4)	-C(19)	108.4 (4)	C(8)	-C(14)	-C(23)	108.7 (3)
C(3)	-C(4)	-C(20)	110.4 (4)	C(13)	-C(14)	-C(23)	108.6 (3)
C(19)	-C(4)	-C(20)	106.7 (4)	C(16)	-C(15)	-C(14)	111.8 (4)
C(6)	-C(5)	-C(4)	113.5 (3)	C(17)	-C(16)	-C(15)	116.3 (4)
C(6)	-C(5)	-C(10)	110.7 (3)	C(18)	-C(17)	-C(16)	110.1 (4)
C(4)	-C(5)	-C(10)	118.3 (3)	C(18)	-C(17)	-C(24)	107.5 (4)
C(7)	-C(6)	-C(5)	114.1 (4)	C(18)	-C(17)	-C(25)	110.5 (4)
C(8)	-C(7)	-C(6)	117.3 (4)	C(16)	-C(17)	-C(24)	109.4 (4)
C(9)	-C(8)	-C(7)	112.3 (4)	C(16)	-C(17)	-C(25)	109.4 (4)
C(9)	-C(8)	-C(14)	115.6 (3)	C(24)	-C(17)	-C(25)	109.9 (4)
C(7)	-C(8)	-C(14)	117.0 (4)	O(3)	-C(18)	-C(13)	120.4 (4)
C(10)	-C(9)	-C(8)	119.1 (3)	O(3)	-C(18)	-C(17)	118.2 (4)
C(10)	-C(9)	-C(11)	120.6 (4)	C(13)	-C(18)	-C(17)	121.3 (4)
C(8)	-C(9)	-C(11)	120.3 (4)	C(26)	-C(25)	-C(17)	116.4 (4)
C(21)	-C(10)	-C(1)	110.2 (3)	C(27)	-C(26)	-C(25)	111.6 (5)
C(21)	-C(10)	-C(5)	114.3 (4)	C(28)	-C(27)	-C(26)	113.9 (5)
C(21)	-C(10)	-C(9)	107.8 (4)	C(29)	-C(28)	-C(27)	113.0 (6)
C(1)	-C(10)	-C(5)	106.0 (3)	C(29)	-C(28)	-C(30)	111.0 (6)
C(1)	-C(10)	-C(9)	109.8 (3)	C(27)	-C(28)	-C(30)	108.2 (6)
C(5)	-C(10)	-C(9)	108.7 (3)	C(32)	-C(31)	-O(1)	113.2 (5)
C(12)	-C(11)	-C(9)	124.6 (4)	C(32)	-C(31)	-O(2)	125.0 (5)
C(13)	-C(12)	-C(11)	112.4 (4)	O(1)	-C(31)	-O(2)	121.8 (5)
C(14)	-C(13)	-C(12)	108.0 (3)	C(3)	-O(1)	-C(31)	118.1 (4)
C(14)	-C(13)	-C(18)	110.5 (3)				

14 and **15** is the first example of the energetically unfavorable rearrangement of triterpenes involving a sequential shift of the multigroup.

TABLE 5. ATOMIC POSITIONAL PARAMETERS $(\times 10)^4$ AND ISOTROPIC TEMPERATURE FACTORS $(\times 10^2)$ FOR NON-HYDROGEN ATOMS OF DIBENZOATE (**20**) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	B_{eq}[a)]
C(1)	5734(2)	5565(2)	36(4)	501(6)
C(2)	6619(2)	5650(2)	−175(4)	538(7)
C(3)	7077(2)	5174(2)	583(4)	466(6)
C(4)	6843(2)	4483(2)	398(4)	459(6)
C(5)	5928(2)	4433(2)	494(4)	406(5)
C(6)	5620(2)	3760(2)	358(4)	497(6)
C(7)	4764(2)	3716(2)	770(4)	473(6)
C(8)	4217(2)	4163(2)	39(4)	445(6)
C(9)	4576(2)	4832(2)	139(4)	437(6)
C(10)	5447(2)	4906(2)	−291(4)	433(6)
C(11)	4007(2)	5323(2)	−412(5)	588(8)
C(12)	3271(3)	5335(2)	381(6)	708(9)
C(13)	2976(2)	4696(2)	769(5)	597(8)
C(14)	3385(2)	4165(2)	622(4)	480(6)
C(15)	3037(2)	3529(2)	949(4)	510(7)
C(16)	3075(2)	3358(2)	2307(4)	455(6)
C(17)	2779(2)	2696(2)	2668(4)	464(6)
C(18)	2167(3)	4722(3)	1327(7)	908(12)
C(19)	1950(2)	2558(2)	2177(5)	553(7)
C(20)	1297(3)	2967(2)	2627(5)	650(9)
C(21)	521(3)	2810(3)	1949(6)	796(11)
C(22)	−167(3)	3172(3)	2369(7)	772(11)
C(23)	7168(3)	4231(2)	−823(5)	678(9)
C(24)	7207(3)	4106(2)	1470(5)	651(8)
C(25)	5525(3)	4824(3)	−1695(4)	632(8)
C(26)	4104(3)	3912(2)	−1283(5)	626(8)
C(27)	3283(2)	2171(2)	2119(5)	526(7)
C(28)	2810(3)	2644(2)	4084(5)	582(7)
C(29)	−512(6)	2804(4)	3521(11)	1491(23)
C(30)	−866(4)	3083(4)	1515(9)	1350(19)
C(31)	8336(2)	5700(2)	592(4)	481(6)
C(32)	9153(2)	5644(2)	118(4)	467(6)
C(33)	9683(3)	6115(2)	431(5)	634(8)
C(34)	10453(3)	6073(3)	−3(6)	770(10)
C(35)	10683(3)	5577(3)	−746(6)	756(10)
C(36)	10152(3)	5120(3)	−1046(6)	720(9)
C(37)	9387(3)	5150(2)	−613(5)	597(8)
C(38)	4600(3)	1840(2)	2125(5)	585(7)
C(39)	5430(3)	2030(2)	2394(5)	596(8)
C(40)	5611(3)	2540(3)	3105(5)	661(9)
C(41)	6392(3)	2689(3)	3331(6)	813(11)
C(42)	6974(3)	2329(4)	2843(6)	893(12)
C(43)	6810(3)	1826(4)	2127(6)	929(13)
C(44)	6025(3)	1660(3)	1872(6)	838(11)
O(1)	7903(1)	5208(1)	253(3)	533(4)
O(2)	8100(2)	6130(1)	1204(3)	629(5)
O(3)	4096(1)	2289(1)	2432(3)	556(5)
O(4)	4410(2)	1349(2)	1680(5)	892(8)

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

The formation of seco-acylal (**22**) is interpreted in terms of mechanism involving 1,2-alkyl migration (*c*) followed by a bond fission (*e*). These skeletal rearrangements appear often in sesquiterpene oxides such as β-patchoulene oxide[15)] or cyperene oxide,[16)] and they also encounter in triterpene epoxides; for example 18,19-epoxylupane derivatives are transformed into 18,19-seco-lup-13(18)-ene (=bacchar-13(18)-ene) derivatives on treatment with $BF_3 \cdot OEt_2$.[17)]

In this rearrangement reaction, a formation of Friedel-Crafts type acetylation products was observed, and these products caused the complication in the separation procedure. Then the backbone rearrangement reaction was examined in benzene.

13β,18β-Epoxybaccharan-3β-yl acetate (**6b**) was treated with $BF_3 \cdot OEt_2$ in benzene at room temperature for 30 min. The reaction product was separated into five compounds by silica-gel chromatography.

The first-eluted compound was shown to be bacchara-11,13(18)-dien-3β-yl acetate (**7**). The second compound was also a known 18-oxobaccharan-3β-yl acetate (**9**),[9)] which was identified with an authentic sample prepared by acetylation of 18-oxobaccharan-3β-ol.[8)]

The third compound showing a singlet signal at δ 9.45 (1H) in the ^{1}H NMR spectrum, was inferred to

TABLE 6. BOND LENGTHS (l/Å) OF DIBENZOATE (**20**) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom 1	Atom 2	Length	Atom 1	Atom 2	Length
C(1)	-C(2)	1.539(6)	C(17)	-C(27)	1.527(6)
C(1)	-C(10)	1.523(6)	C(17)	-C(28)	1.545(7)
C(2)	-C(3)	1.519(6)	C(19)	-C(20)	1.494(6)
C(3)	-C(4)	1.531(6)	C(20)	-C(21)	1.551(7)
C(3)	-O(1)	1.457(4)	C(21)	-C(22)	1.476(8)
C(4)	-C(5)	1.569(5)	C(22)	-C(29)	1.588(13)
C(4)	-C(23)	1.535(7)	C(22)	-C(30)	1.524(10)
C(4)	-C(24)	1.544(7)	C(27)	-O(3)	1.450(5)
C(5)	-C(6)	1.528(5)	C(31)	-C(32)	1.491(6)
C(5)	-C(10)	1.551(5)	C(31)	-O(1)	1.330(5)
C(6)	-C(7)	1.531(5)	C(31)	-O(2)	1.198(5)
C(7)	-C(8)	1.548(6)	C(32)	-C(33)	1.390(6)
C(8)	-C(9)	1.548(6)	C(32)	-C(37)	1.373(6)
C(8)	-C(14)	1.557(5)	C(33)	-C(34)	1.401(7)
C(8)	-C(26)	1.544(6)	C(34)	-C(35)	1.382(8)
C(9)	-C(10)	1.567(5)	C(35)	-C(36)	1.366(8)
C(9)	-C(11)	1.544(6)	C(36)	-C(37)	1.390(7)
C(10)	-C(25)	1.542(6)	C(38)	-C(39)	1.502(6)
C(11)	-C(12)	1.525(7)	C(38)	-O(3)	1.327(5)
C(12)	-C(13)	1.506(7)	C(38)	-O(4)	1.193(6)
C(13)	-C(14)	1.332(6)	C(39)	-C(40)	1.364(7)
C(13)	-C(18)	1.509(7)	C(39)	-C(44)	1.403(8)
C(14)	-C(15)	1.515(6)	C(40)	-C(41)	1.392(7)
C(15)	-C(16)	1.521(6)	C(41)	-C(42)	1.360(9)
C(16)	-C(17)	1.543(6)	C(42)	-C(43)	1.350(10)
C(17)	-C(19)	1.541(6)	C(43)	-C(44)	1.413(8)

Table 7. Bond angles (ϕ/°) of dibenzoate (**20**) with estimated standard deviations in parentheses

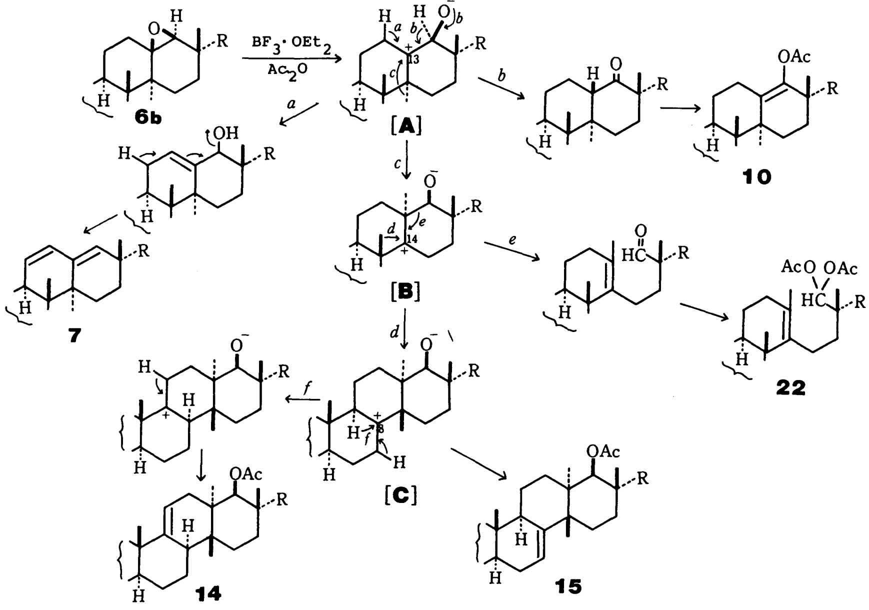
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Aangle
C(2)	-C(1)	-C(10)	112.9 (3)	C(16)	-C(15)	-C(14)	114.9 (3)
C(3)	-C(2)	-C(1)	110.4 (3)	C(17)	-C(16)	-C(15)	116.7 (3)
C(4)	-C(3)	-C(2)	115.4 (3)	C(19)	-C(17)	-C(16)	112.7 (3)
C(4)	-C(3)	-O(1)	105.4 (3)	C(19)	-C(17)	-C(27)	104.1 (3)
C(2)	-C(3)	-O(1)	109.4 (3)	C(19)	-C(17)	-C(28)	111.3 (3)
C(5)	-C(4)	-C(3)	108.4 (3)	C(16)	-C(17)	-C(27)	112.2 (3)
C(5)	-C(4)	-C(23)	113.2 (3)	C(16)	-C(17)	-C(28)	107.9 (3)
C(5)	-C(4)	-C(24)	108.4 (3)	C(27)	-C(17)	-C(28)	108.6 (3)
C(3)	-C(4)	-C(23)	110.7 (3)	C(20)	-C(19)	-C(17)	117.5 (4)
C(3)	-C(4)	-C(24)	106.9 (3)	C(21)	-C(20)	-C(19)	111.0 (4)
C(23)	-C(4)	-C(24)	109.1 (4)	C(22)	-C(21)	-C(20)	114.9 (5)
C(6)	-C(5)	-C(4)	113.6 (3)	C(29)	-C(22)	-C(21)	106.4 (6)
C(6)	-C(5)	-C(10)	111.5 (3)	C(29)	-C(22)	-C(30)	97.4 (6)
C(4)	-C(5)	-C(10)	116.6 (3)	C(21)	-C(22)	-C(30)	111.8 (6)
C(7)	-C(6)	-C(5)	111.0 (3)	O(3)	-C(27)	-C(17)	108.7 (3)
C(8)	-C(7)	-C(6)	112.8 (3)	C(32)	-C(31)	-O(1)	111.2 (3)
C(9)	-C(8)	-C(7)	106.6 (3)	C(32)	-C(31)	-O(2)	124.5 (4)
C(9)	-C(8)	-C(14)	109.2 (3)	O(1)	-C(31)	-O(2)	124.3 (4)
C(9)	-C(8)	-C(26)	115.5 (3)	C(33)	-C(32)	-C(31)	117.8 (4)
C(7)	-C(8)	-C(14)	110.1 (3)	C(33)	-C(32)	-C(37)	120.0 (4)
C(7)	-C(8)	-C(26)	110.0 (3)	C(31)	-C(32)	-C(37)	122.2 (4)
C(14)	-C(8)	-C(26)	105.4 (3)	C(34)	-C(33)	-C(32)	118.9 (5)
C(10)	-C(9)	-C(8)	116.5 (3)	C(35)	-C(34)	-C(33)	120.8 (5)
C(10)	-C(9)	-C(11)	114.4 (3)	C(36)	-C(35)	-C(34)	119.3 (5)
C(8)	-C(9)	-C(11)	110.0 (3)	C(37)	-C(36)	-C(35)	120.7 (5)
C(25)	-C(10)	-C(1)	107.8 (3)	C(32)	-C(37)	-C(36)	120.3 (4)
C(25)	-C(10)	-C(5)	115.2 (3)	C(39)	-C(38)	-O(3)	111.7 (4)
C(25)	-C(10)	-C(9)	111.5 (3)	C(39)	-C(38)	-O(4)	124.8 (5)
C(1)	-C(10)	-C(5)	107.1 (3)	O(3)	-C(38)	-O(4)	123.5 (5)
C(1)	-C(10)	-C(9)	109.1 (3)	C(40)	-C(39)	-C(38)	122.5 (4)
C(5)	-C(10)	-C(9)	106.0 (3)	C(40)	-C(39)	-C(44)	120.5 (5)
C(12)	-C(11)	-C(9)	108.1 (4)	C(38)	-C(39)	-C(44)	117.0 (5)
C(13)	-C(12)	-C(11)	114.7 (4)	C(41)	-C(40)	-C(39)	119.8 (5)
C(14)	-C(13)	-C(12)	123.4 (4)	C(42)	-C(41)	-C(40)	120.2 (6)
C(14)	-C(13)	-C(18)	123.9 (5)	C(43)	-C(42)	-C(41)	121.1 (6)
C(12)	-C(13)	-C(18)	112.6 (4)	C(44)	-C(43)	-C(42)	120.5 (6)
C(15)	-C(14)	-C(8)	116.7 (3)	C(39)	-C(44)	-C(43)	117.9 (5)
C(15)	-C(14)	-C(13)	121.2 (4)	C(3)	-O(1)	-C(31)	120.5 (3)
C(8)	-C(14)	-C(13)	122.0 (4)	C(27)	-O(3)	-C(38)	116.0 (3)

be an aldehyde (**21**) with the secobaccharene skeleton, the structure of which was confirmed by chemical conversion into *D*-friedo-13,18-secobacchar-13-ene-3β,18-diol (**16**) by lithium aluminium hydride-reduction. Therefore, the structure of the third compound was determined to be 3β-acetoxy-*D*-friedo-13,18-secobacchar-13-en-18-al (**21**).

The fourth compound (δ 3.33 (1H, s), 4.46 (1H, dd), and 5.35 (1H, m); *m/z* 486, 301, and 289) and the fifth compound (δ 3.34 (1H, s), 4.47 (1H, dd), and 5.31 (1H, m); *m/z* 486, 301, and 289) were suggested to be 18β-hydroxy-*D*:*C*-friedobacchar-9(11)- and -7-en-3β-yl acetates (**23** and **24**), respectively from the spectral data. These compounds were found to be identical with those obtained by acetylation of the corresponding diols (**11** and **12**), respectively.

Previously we reported that the $BF_3 \cdot OEt_2$-catalyzed backbone rearrangement of 3,4-epoxytriterpenes in solvents with low nucleophilicity proceeds up to C, D, or E ring to give 12-, 18-, or 19-ene derivative, while the rearrangement in solvents with high nucleophilicity, such as diethyl ether or tetrahydrofuran, is interupted in early stage to afford *D*:*A*- or *D*:*B*-friedo type triterpenes preferentially.[10,11,18–20] In order to examine the migratory aptitude, the epoxide (**6b**) was treated with $BF_3 \cdot OEt_2$ in various solvents and the results were summarized in Table 8.

In backbone rearrangement reactions in the



Scheme 1.

Table 8. Relative amount ratios of products in the reaction of 13β,18β-epoxide (**6b**) with $BF_3 \cdot OEt_2$ at room temperature

Solvent	Reaction time (min)	diene (**7**)	18-one (**9**)	18-al (**21**)	9(11)-ene (**23**)	7-ene (**24**)
Hexane[a]	30	25	15	10	30	20
Benzene[b]	30	50	17	7	16	10
Dichloromethane[a]	30	55	15	10	15	5
Acetonitrile[a]	30	60	10	5	15	10
Diethyl ether[b]	60	60	15	6	3	10
Tetrahydrofuran[a]	180	80	Trace	Trace	10	Trace
Acetic anhydride[b]	120	14	31[c]	15[c]	31[c]	9[c]

a) Determined by GLC. b) Calculated from isolated yield. c) The reaction products are the corresponding acetates or acylal.

energetically unfavorable direction, it is anticipated that the effects of the nucleophilicity of the solvents on the degree of the rearrangement were larger than in energetically favorable rearrangements. In fact, the table showed that relative yields of thermodynamically unfavorable products (**23** and **24**) increased in hexane and benzene, while they decreased in diethyl ether and tetrahydrofuran. Furthermore, it is also proved that acetic anhydride is a useful solvent which enables the effective backbone rearrangement.

Experimental

General Procedures. Melting points were measured on a Mel-temp capillary melting point apparatus (Laboratory Devices) and are uncorrected. IR spectra were measured with a Hitachi 260-30 spectrometer, mass spectra with a JMS-D300 (JEOL) mass spectrometer at 70 eV with a direct inlet system, and ^1H NMR spectra with a Varian EM-390 (90 MHz) spectrometer. Chemical shifts are expressed in δ (ppm downfield from TMS as an internal standard) and coupling constants in Hz. GLC analysis was carried out on a Shimadzu Gas Chromatograph GC-6A equipped with a hydrogen-flame ionization detector. Thin-layer chromatography was carried out on Kieselgel 60 GF_{254} (E. Merck) coated in 0.25 mm-thickness (for analytical) and in 0.5 mm-thickness (for preparative). Wakogel C-200 (Wako) was used for silica-gel column chromatography.

Treatment of Bacchar-13(18)-en-3β-yl Acetate (1) with Hydrogen Chloride. A solution of bacchar-13(18)-en-3β-yl acetate (**1**; 27.8 mg) in chloroform (30 ml) was saturated with dry hydrogen chloride and the solution was stirred for 22 h at room temperature. After the usual work-up, the reaction product was examined by GLC (column: Dexsil-300GC, temperature: 270—300 °C (5 °C/min), N_2: 60 ml/min) and was shown to be a 1:1 mixture of 13(18)-ene (**1**) and 12-ene (**2**). The retention times were 9.3 and 11.3 min for **1** and **2**, respectively.

Epoxyidation of Bacchar-13(18)-en-3β-yl Acetate (1). Bacchar-13(18)-en-3β-yl acetate (**1**; 114 mg) was dissolved in dichloromethane (5 ml) and the solution was stirred with

MCPBA (110 mg) and sodium hydrogencarbonate (300 mg) at room temperature. The reaction product was treated with a sodium hydrogensulfite solution, worked-up usually, and was subjected to separation by column chromatography on silica gel (120 g). Elution with hexane–ether (96:4) gave 13α,18α-epoxide (**6a**; 10 mg) and 13β,18β-epoxide (**6b**; 95 mg). **6a**: mp 182—183 °C (from $CHCl_3$-MeOH); IR (KBr) 1735 and 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.0 (3H, s, Ac), 2.3 (1H, s, 18β-H), and 4.5 (1H, m, 3α-H); MS *m/z* (%) 486 (M^+; 63), 468 (21), and 383 (100); Found: *m/z* 486.4020. Calcd for $C_{32}H_{54}O_3$: M, 486.4071. **6b**: mp 130.5—131.5 °C (from $CHCl_3$-MeOH); IR (KBr) 1740 and 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.0 (3H, s, Ac), 2.65 (1H, s, 18α-H), and 4.5 (1H, m, 3α-H); MS *m/z* (%) 486 (M^+, 35), 468 (92), 383 (100); Found: *m/z* 486.4046. Calcd for $C_{32}H_{54}O_3$; M, 486.4071.

*Backbone Rearrangement of 13β,18β-Epoxybaccharan-3β-yl Acetate (**6b**) in Acetic Anhydride.* 13β,18β-Epoxybaccharan-3β-yl acetate (**6b**; 230 mg) was dissolved in freshly distilled acetic anhydride (50 ml). To the solution kept at 0 °C, $BF_3\cdot OEt_2$ (0.2 ml) was added and the stirring was continued for 2 h. The reaction product was then poured into a cold mixture of a saturated sodium hydrogencarbonate solution (50 ml) and ether (200 ml) with vigorous stirring and the ethereal layer was separated. The aqueous layer was extracted with ether and the ethereal extract was combined with the ether layer, washed with brine, and dried over sodium sulfate. The organic extract, after evaporation, was dissolved in hexane and the solution was charged on a column of silica gel (25 g) covered with Florisil (2 g). Elution was performed with 5% ethyl acetate in hexane and 19 fractions (each 50 ml) were collected. Fractions 4 and 5, fractions 6—10, and fractions 14—19 afforded, on evaporation, fractions **A** (20 mg), **B** (115 mg), and **C** (80 mg), respectively.

The fraction **A** was identical with an authentic bacchara-11,13(18)-dien-3β-yl acetate (**7**)[6] in every respect.

*Hydrolysis and Separation of Fraction **B**.* The fraction **B** (115 mg), dissolved in tetrahydrofuran (THF) (15 ml), was heated with lithium aluminium hydride (LAH) (25 mg) at reflux for 30 min. The reaction product was worked up as usual and subjected to separation by column chromatography on silica gel (10 g). Elution with 10% ethyl acetate in hexane gave a mixture (*ca.* 100 mg) of compound $\mathbf{B_1}$ (**8**) and compound $\mathbf{B_2}$ (**11**) (fractions 15—18, each 20 ml) and compound $\mathbf{B_3}$ (**12**; 11.5 mg, fractions 19—22). The mixture was subjected to further separation by column chromatography on silica gel (5 g) and eluted with hexane–dichloromethane–ethyl acetate (20:20:1) to afford **8** (42 mg) and **11** (42 mg). Baccharane-3β,18α-diol (**8**): mp 164—167 °C (from Et_2O-MeOH); IR (Nujol) 3500 and 3350 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.2 (1H, m) and 3.25 (1H, br s); MS *m/z* 446 (M^+), 428, 410, and 95 (base peak); Found: *m/z* 446.4190. Calcd for $C_{30}H_{54}O_2$: M, 446.4123. *D*:*C*-Friedobacchar-9(11)-ene-3β,18β-diol (**11**): mp *ca.* 202 °C (decomp) (from MeOH); IR (Nujol) 3450—3400 cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.21 (1H, dd, *J*=10 and 6 Hz; $C_{(3\alpha)}$-H), 3.38 (1H, s; $C_{(18\alpha)}$-H), and 5.38 (1H, m; $C_{(11)}$-H); MS *m/z* 444 (M^+), 429, 411, 408, 393 (base peak), 259, 247, 241, and 229; Found: *m/z* 444.3959. Calcd for $C_{30}H_{52}O_2$: M, 444.3967. *D*:*C*-Friedobacchar-7-ene-3β,18β-diol (**12**): mp 230—233 °C (from MeOH); IR (film) 3430 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.24 (1H, dd, *J*=9 and 6 Hz; $C_{(3\alpha)}$-H), 3.34 (1H, s; $C_{(18\alpha)}$-H, and 5.35 (1H, m; $C_{(7)}$-H); MS *m/z* 444 (M^+), 429, 426, 411, 408, 393, 383, 259 (base peak), 247, 241, and 229.

*Hydrolysis and Separation of Fraction **C**.* The fraction **C** (80 mg) was dissolved in THF (10 ml) and treated with LAH (20 mg) at reflux temperature for 30 min. The reaction product was worked up as before to afford an oily residue (70 mg), which was subjected to separation by column chromatography on silica gel (4 g). Elution with 10% ethyl acetate in hexane gave compound $\mathbf{C_1}$ (**16**; 20 mg), 20% ethyl acetate in hexane a mixture $\mathbf{C_2}$ (25 mg), and 33% ethyl acetate in hexane compound $\mathbf{C_3}$ (16 mg), respectively.

Compound $\mathbf{C_1}$, *D*-friedo-13,18-secobacchar-13-ene-3β,18-diol (**16**): mp 99—103 °C (from MeOH); IR (Nujol) 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.55 (3H, s; $C_{(13)}$-CH_3), 3.17 (1H, dd, *J*=9 and 6 Hz; $C_{(3\alpha)}$-H) and 3.36 (2H, s, CH_2-OH); MS *m/z* 446 (M^+), 431, 428, 413, 275 (base peak), and 257; Found: *m/z* 446.4088. Calcd for $C_{30}H_{54}O_2$: M, 446.4121.

Since the compound $\mathbf{C_2}$ was found to be a complex mixture of compounds derived from acetylated rearranged products, further examination was not carried out.

Compound $\mathbf{C_3}$: IR (Nujol) 3380 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.23 (1H, dd, *J*=10 and 6 Hz; $C_{(3\alpha)}$-H), 3.32 (1H, s; $C_{(18\alpha)}$-H), and 4.20 (1H, m; -$CH(OH)CH_3$); MS *m/z* 488 (M^+), 443, 429, 425, 407, 397, and 223.

*18-Oxo-*D:C*-friedobacchar-9(11)-en-3β-yl Acetate (**13**).* *D*:*C*-Friedobacchar-9(11)-ene-3β,18β-diol (**11**; 43 mg) was treated with acetic anhydride and pyridine at room temperature overnight to afford a diacetate (**14**; 6.5 mg) and a monoacetate (**23**; 30 mg). Diacetate (**14**): mp 179.5—181 °C (from MeOH); IR (Nujol) 1745, 1735, and 1245 cm^{-1}. ^1H NMR ($CDCl_3$) δ=2.02 and 2.06 (each 3H, s; OAc), 4.50 (1H, m; $C_{(3\alpha)}$-H), 4.90 (1H, s; $C_{(18\alpha)}$-H), and 5.35 (1H, m; $C_{(11)}$-H); MS *m/z* 528 (M^+), 513, 468 (base peak), 453, 393, 301, and 241; Found: *m/z* 528.4124. Calcd for $C_{34}H_{56}O_4$. Monoacetate (**23**): mp 244—248 °C (from $CHCl_3$-MeOH), IR (Nujol) 3550 and 1740 cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.33 (1H, s; $C_{(18\alpha)}$-H), 4.46 (1H, dd, *J*=9 and 6 Hz; $C_{(3\alpha)}$-H), and 5.35 (1H, m; $C_{(11)}$-H); MS *m/z* 486 (M^+), 471, 453, 426, 411, 393, 383, 301 (base peak), 289, 241, and 229; Found: *m/z* 486.4028. Calcd for $C_{32}H_{54}O_3$: M, 486.4073.

The monoacetate (**23**; 29 mg) in acetone (10 ml) was oxidized with Jones reagent (0.05 ml) at 0 °C for 20 min. The usual work-up and crystallization from chloroform–methanol gave a keto acetate (**13**; 9 mg), mp 115.5—117.5 °C; IR (film) 1740, 1692, and 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.05 (3H, s; OAc), 4.47 (1H, dd, *J*=10 and 6 Hz; $C_{(3\alpha)}$-H), and 5.38 (1H, m; $C_{(11)}$-H); MS *m/z* 484 (M^+), 469, 409, 400, 344, and 343 (base peak); Found: *m/z* 484.3919. Calcd for $C_{32}H_{52}O_3$: M, 484.3917.

D*-Friedo-13,18-secobacchar-13-ene-3β,18-diyl Diacetate (**17**).* Acetylation of a diol (**16**) by the usual procedure gave a diacetate (**17**) as an oily material, IR (film) 1745 and 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.53 (3H, s; $C_{(13)}$-CH_3), 2.04 (6H, s; 2×OAc), 3.82 (2H, s; -CH_2-OAc), and 4.46 (1H, dd, *J*=9 and 6 Hz; $C_{(3\alpha)}$-H); MS *m/z* 530 (M^+), 470, 455, 395, 317 (base peak), and 257; Found: *m/z* 530.4261. Calcd for $C_{34}H_{58}O_4$: M, 530.4333.

D*-Friedo-13,18-secobacchar-13-ene-3β,18-diyl Dibenzoate (**20**).* A diol (**16**; 5 mg) was treated with benzoyl chloride and pyridine at room temperature for 6 h. The usual work-up and crystallization from chloroform–methanol gave a dibenzoate (**20**; 2.5 mg), mp 135.5—137.5 °C; IR (film) 1715, 1280, 1120, and 720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.53 (3H, s; C$_{(13)}$-CH$_3$), 4.07 (2H, brs; *C*H$_2$-OBz) 4.63 (1H, dd, *J*=9 and 6 Hz; C$_{(3\alpha)}$-H), and 7.9—8.1 (10H; aromatic protons); MS *m/z* 532 (M$-$C$_6$H$_5$COOH)$^+$, 517, 489, 410 (M$-$2×C$_6$H$_5$COOH)$^+$, 395, 257, and 57 (base peak); High resolution MS *m/z* 532.4278. Calcd for C$_{37}$H$_{56}$O$_2$ (M$-$C$_6$H$_5$COOH): *m/z* 532.4278.

*Methyl 3-Oxo-*D*-friedo-13,18-secobacchar-13-en-18-oate (18).* A solution of a diol (**16**; 10 mg) in acetone was treated with an excess of Jones reagent. After addition of isopropyl alcohol, the reaction mixture was filtered through a column of Florisil. The filtrate gave, on evaporation, a keto carboxylic acid, which was dissolved in ether and methylated with diazomethane. The reaction product was purified by column chromatography on silica gel, eluted with 10% ethyl acetate in hexane to afford a keto methyl ester (**18**; 5 mg), IR (film) 1730 and 1705 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.53 (3H, s; C$_{(13)}$-CH$_3$), 2.35—2.6 (2H; C$_{(2)}$-H$_2$) and 3.67 (3H, s; -COOCH$_3$); MS *m/z* 472 (M$^+$), 440, 412, 384, 343, 315, 291, and 69 (base peak).

Backbone Rearrangement of 13β,18β-Epoxybaccharan-3β-yl Acetate (6b) in Benzene. A solution of 13β,18β-epoxide (**6b**; 115 mg) in dry benzene (5 ml) was treated with BF$_3$·OEt$_2$ (0.02 ml) at room temperature for 30 min with stirring. The reaction product was worked up as before and separated by column chromatography on silica gel (4 g). Bacchara-11,13(18)-dien-3β-yl acetate (**7**; 58.5 mg) was eluted with 3% ethyl acetate in hexane. Elution with 5% ethyl acetate in hexane gave 18-oxobaccharan-3β-yl acetate (**9**; 18.8 mg) and an aldehyde (**21**; 7.3 mg), and elution with 10% ethyl acetate in hexane gave 18β-hydroxy-*D*:*C*-friedobacchar-9(11)-en-3β-yl acetate (**23**; 17.8 mg) and its 7-ene isomer (**24**; 11.5 mg). 18-Oxobaccharan-3β-yl acetate (**9**):[9] mp 184.5—186 °C (from CHCl$_3$-MeOH); IR (Nujol) 1725, 1700, and 1245 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.67 (1H, m; C$_{(17)}$-H) and 4.47 (1H, dd, *J*=10 and 6 Hz; C$_{(3\alpha)}$-H); MS *m/z* 486 (M$^+$), 468, 426, 411, 408, and 402; Found: *m/z* 486.4111. Calcd for C$_{32}$H$_{54}$O$_3$: M, 486.4073. Aldehyde (**21**): ^{1}H NMR (CDCl$_3$) δ=1.52 (3H, s; C$_{(13)}$-CH$_3$), 2.03 (3H, s; C$_{(3\beta)}$-OAc), 4.46 (1H, dd, *J*=9 and 6 Hz; C$_{(3\alpha)}$-H), and 9.45 (1H, s; C$_{(17)}$-CHO). The aldehyde (**21**; 5 mg) was converted into a diol (**16**) by reduction with LAH (5 mg). 18β-Hydroxy-*D*:*C*-friedobacchar-9(11)-en-3β-yl acetate (**23**): mp 244—248 °C (from CHCl$_3$-MeOH); IR (Nujol) 3350 and 1740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.0 (3H, s; C$_{(3\beta)}$-OAc), 3.33 (1H, s, C$_{(18\alpha)}$-H), 4.46 (1H, dd, *J*=9 and 6 Hz; C$_{(3\alpha)}$-H), and 5.35 (1H, m; C$_{(11)}$-H); MS *m/z* 486 (M$^+$), 471, 453, 426, 411, 393, 383, 301, 289, 241 (base peak), and 229; Found: *m/z* 486.4028. Calcd for C$_{32}$H$_{54}$O$_3$: M, 486.4073. 18β-Hydroxy-*D*:*C*-friedobacchar-7-en-3β-yl acetate (**24**): mp 77—78 °C (from MeOH); IR (Nujol) 3550, 1725, and 1245 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.03 (3H, s; C$_{(3\beta)}$-OAc), 3.34 (1H, s; C$_{(18\alpha)}$-H), 4.47 (1H, m; C$_{(3\alpha)}$-H), and 5.31 (1H, m; C$_{(7)}$-H); MS *m/z* 486 (M$^+$), 471, 411, 301, 289, 241, and 229; Found: *m/z* 486.4084. Calcd for C$_{32}$H$_{54}$O$_3$: M, 486.4073.

Acetylation of Diols (11 and 12). Diols (**11** and **12**) were acetylated with acetic anhydride and pyridine at room temperature to afford acetates (**23** and **24**), respectively, which were identifid by ^{1}H NMR, MS, and TLC.

Backbone Rearrangement of 13β,18β-Epoxybaccharan-3β-yl Acetate (6b) in Diethyl Ether and in Other Solvents. 13β,18β-Epoxide (**6b**; 30 mg) was treated with BF$_3$·OEt$_2$ in diethyl ether and the usual work-up and separation by chromatography gave a diene (**7**; 18 mg), a ketone (**9**; 4.5 mg), an aldehyde (**21**; 1 mg), 9(11)-en (**23**; 1 mg), and 7-ene (**24**; 3 mg).

A small amount of 13β,18β-epoxide (**6b**) was treated with BF$_3$·OEt$_2$ in hexane, dichloromethane, acetonitrile, and THF, respectively, and each reaction product, after the usual work-up, was examined by GLC (column: Dexsil-300GC, temperature: 240—290 °C (5 °C/min)). The relative yields of products were given in Table 8 and their retention times were 9.0, 10.6, 13.5, 14.1, and 14.9 min for **7**, **21**, **24**, **9**, and **23**, respectively.

References

1) A preliminary account of this report: K. Suemura, T. Irokawa, M. Tori, S. Ohta, Y. Moriyama, T. Tsuyuki, T. Takahashi, A. Itai, and Y. Iitaka, *Chem. Lett.*, **1982**, 1617.

2) *e.g.* R. M. Coates, *Fortschr. Chem. Org. Naturst.*, **33**, 74 (1976).

3) I. Agata, E. J. Corey, A. G. Hortmann, J. Klein, S. Proskow, and J. J. Ursprung, *J. Org. Chem.*, **30**, 1698 (1965).

4) a) Z. Paryzek, *J. Chem. Soc., Perkin Trans., 1*, **1979**, 1222; b) *Tetrahedron Lett.*, **1976**, 4761.

5) G. V. Baddeley, H. J. Samaan, J. H. Simes, and T. H. Ai, *J. Chem. Soc., Perkin Trans., 1*, **1979**, 7.

6) L. Cattel, L. Delprino, and A. Dietsch, *Gazz. Chim. Ital.*, **109**, 705 (1979).

7) K. Masuda, K. Shiojima, and H. Ageta, *Chem. Pharm. Bull.*, **31**, 2530 (1983).

8) S. Ohta, M. Tori, T. Tsuyuki, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **56**, 2187 (1983).

9) E. Suokas and T. Hase, *Acta Chem. Scand.*, **25**, 2359 (1971).

10) K. Tachibana, M. Tori, Y. Moriyama, T. Tsuyuki, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **50**, 1552 (1977).

11) M. Tori, T. Torii, K. Tachibana, S. Yamada, T. Tsuyuki, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **50**, 469 (1977).

12) H. Ageta, K. Shiojima, K. Masuda, and T. Lin, *Tetrahedron Lett.*, **1981**, 2289.

13) H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Am. Chem. Soc*, **85**, 3688 (1963).

14) The complete F_o—F_c data, anisotropic thermal parameters for non-hydrogen atoms, atomic positional parameters and isotropic thermal parameters for hydrogen atoms, and bond lengths and bond angles containing hydrogen atoms are deposited as Document Nos. 8544 and 8545 for **13** and **20**, respectively, at the Office of the Editor of Bull. Chem. Soc. Jpn.

15) L. Bang, I. G. Guest, and G. Ourisson, *Tetrahedron Lett.*, **1972**, 2089.

16) L. Bang and G. Ourisson, *Tetrahedron Lett.*, **1969**, 3761; *Tetrahedron*, **29**, 2097 (1973).

17) E. Suokas and T. Hase, *Acta Chim. Scand.*, *B* **31**, 231 and 633 (1977).

18) M. Tori, T. Tsuyuki, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **50**, 3381 (1977).

19) S. Yamada, S. Yamada, K. Tachibana, Y. Moriyama, Y. Tanahashi, T. Tsuyuki, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **49**, 1134 (1976).

20) Y. Yokoyama, Y. Moriyama, T. Tsuyuki, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **54**, 234 (1981).