[Chem. Pharm. Bull. 23(1) 98—105 (1975)] UDC 547.597.04

Triterpenoid Chemistry. VIII.[1] Stereospecific Reactions of Triterpenoid 1,3-Glycol Monotosylates and Ketotosylates[2]

Yoshisuke Tsuda,[3a] Kimiaki Isobe, Takehiro Sano,[3] and Akira Morimoto[3b]

Showa College of Pharmaceutical Sciences[3]

(Received June 8, 1974)

The reactions of 1,3-glycol monotosylates of the configurations **A**—**D** with base and LAH were discussed. On reaction with *t*-butoxide, **A** and **D** (cis relationship between –OH and $-CH_2OTs$) gave oxetanes **E** and **F** respectively, while **B** and **C** (trans relationship between these groups) gave the same seco-aldehyde **G**. On LAH reduction, in addition to the above reaction (oxetane formation from **A** and **D**, seco-alcohol formation from **B** and **C**), two further reactions took place; *a*) S–O fission (formation of the glycols **A**—**D**), and *b*) C–O fission (formation of the deoxy-compounds **H** and **I**), for the latter reaction the cyclic intermediate (**K**—**M**) were proposed. The monotosylate of **B** did not give deoxy-compound. The corresponding keto-tosylate (**N** and **O**), when treated with lithium aluminum hydride firstly gave 3β-alcohols (**A** and **C**) which are further reduced as above; the fact which therefore opened a way to yield deoxy-compound (**I**) from type **B** glycol (**B**→**N**→**I**).

A popular system occurring in poly-functional triterpenoid carries hydroxyl groups at C_3 and at one of 4,4-dimethyl group, whose stereochemistry is classified into four types **A**—**D** (Chart 2). Determination of the stereochemistry of these groups is sometimes troublesome by the reasons already mentioned.[1] In the preceeding paper we presented one of a reliable method for this purpose by converting this system to the corresponding acetonide. Here we present further example of chemical method which gives clear cut evidence to determine the stereochemistry of these groups. The method is principally based on the stereospecific reaction of monotosylate of the above 1,3-glycol system with base or with hydride.

We chose the following triperpenoids as models for checking generality of the reactions described below; serratriol[4] for type **A**, lycoclavanol[4] for type **B**, hederagenin for type **C**, and 3-epihederagenin[1] for type **D**.

The corresponding monotosylates were easily obtained from the respective diols by tosylation with tosyl chloride and pyridine at low temperature and rapid chromatographic separation of the product over acid-washed alumina from the accompanying ditosylates; slow chromatography caused further change on some of monotosylates (see below).

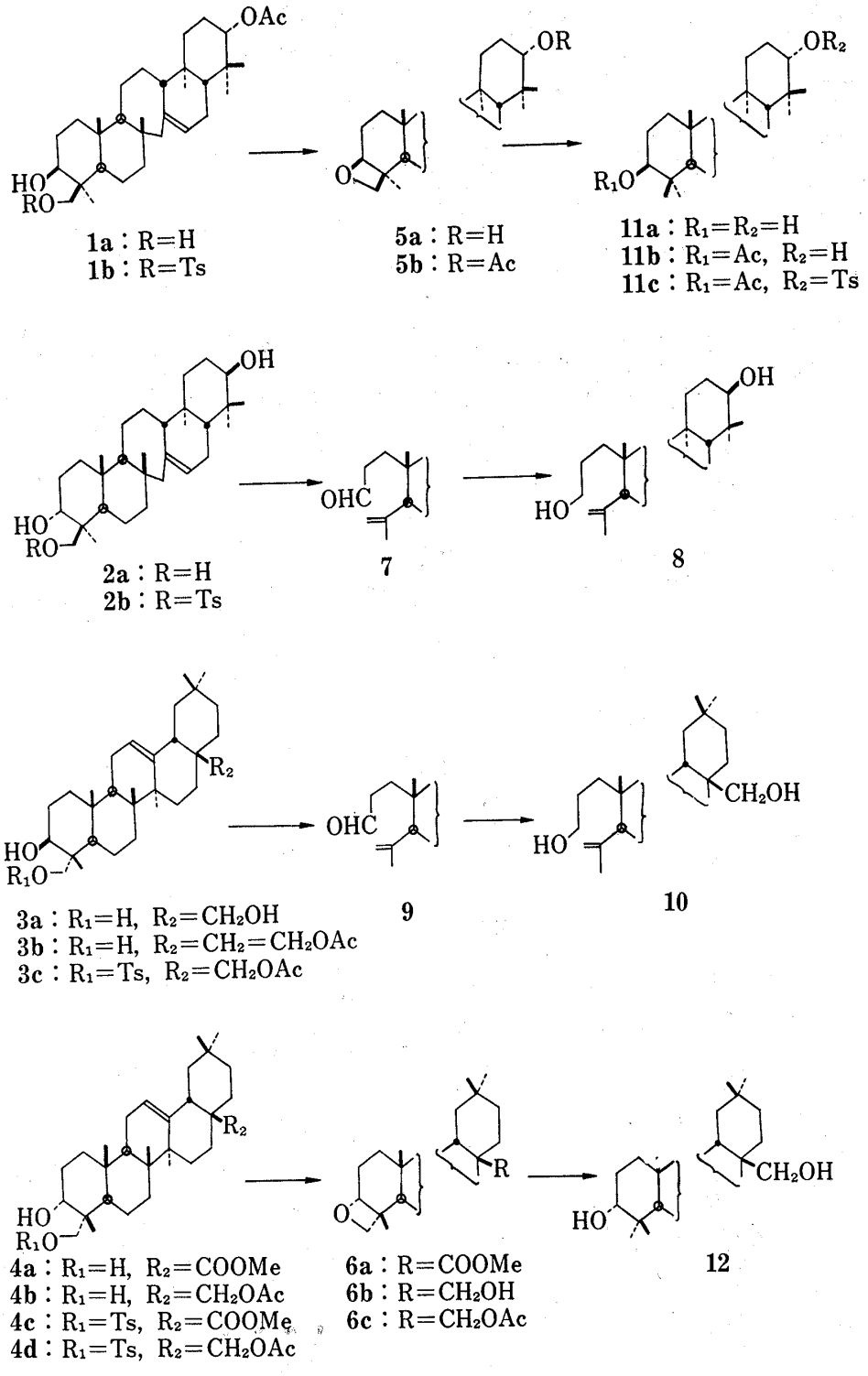
Reaction of 1,3-Glycol Monotosylates with Potassium *t*-Butoxide

When monotosylates **A**—**D** were treated with excess of *t*-BuOK in benzene or in *t*-BuOH at room temperature, each compound rapidly lost toluenesulfonic acid and changed quantitatively into new compounds. Products fall into two groups depending on stereochemistry of the original glycols.

1) Part VII: Y. Tsuda, T. Sano, K. Isobe, and M. Miyauchi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2396 (1974).
2) Works in this paper were presented at the 90th Annual Meeting of Pharmaceutical Society of Japan, Sapporo, July, 1970, 9P-10-3, and at the 14th Symposium on the Chemistry of Natural Products, Fukuoka, Oct. 1970.
3) Location: *Tsurumaki 5-1-8, Setagaya-ku, Tokyo, 154, Japan*; *a*) From whom reprints may be obtained; *b*) Present address: *Takeda Chemical Industries, Ltd.*
4) Y. Tsuda, T. Sano, M. Hatanaka, A. Morimoto, and Y. Inubushi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2383 (1974).

The Monotosylate (**1b**) (type **A**) which has cis relationship between –OH and $-CH_2OTs$ group afforded the oxetane (**5a**)[4] as a sole product, which must be formed by nucleophilic substitution of the tosyloxy group for the hydroxylate ion as illustrated in Chart 2. Alumina, even acid-washed, also caused this cyclization. During chromatographic purification of the monotosylate (**1b**), the oxetane (**5b**) was appeared when the tosylate was slowly passed through alumina by using a non-polar solvent.

In the other cis diol (type **D**), the monotosylate (**4d**) was more reactive and changed appreciably into the oxetane (**6c**) during the process of alumina chromatography. In agreement,



1a : R=H
1b : R=Ts

5a : R=H
5b : R=Ac

11a : $R_1=R_2=H$
11b : $R_1=Ac$, $R_2=H$
11c : $R_1=Ac$, $R_2=Ts$

2a : R=H
2b : R=Ts

7

8

3a : $R_1=H$, $R_2=CH_2OH$
3b : $R_1=H$, $R_2=CH_2=CH_2OAc$
3c : $R_1=Ts$, $R_2=CH_2OAc$

9

10

4a : $R_1=H$, $R_2=COOMe$
4b : $R_1=H$, $R_2=CH_2OAc$
4c : $R_1=Ts$, $R_2=COOMe$
4d : $R_1=Ts$, $R_2=CH_2OAc$

6a : R=COOMe
6b : $R=CH_2OH$
6c : $R=CH_2OAc$

12

Chart 1

the monotosylate was smoothly converted to the oxetane (**6c**) by action of *t*-butoxide, the structure of which was confirmed by the nuclear magnetic resonance (NMR) spectrum, exhibiting an AB quartet at δ 3.91 ($-CH_2-O-$) and a broad singlet at δ 4.71 ($>CH-O-$).

In contrast, lycoclavanol monotosylate (**2b**) (type **B**) which has *trans*-diaxial relationship between the above mentioned two groups afforded entirely different result; the product was an A-seco-aldehyde (**7**) which was well characterized by converting it into the corresponding seco-alcohol (**8**) by adding methanolic sodium borohydride to the reaction mixture, since the seco-aldehyde (**7**) was vulnerable to aerial oxidation in the presence of strong base. Triplet at δ 3.63 due to $-CH_2-C\underline{H}_2-OH$, two broad singlets at δ 4.71 and 4.88 due to $>C=C\underline{H}_2$ together with infrared (IR) bands at 892 cm^{-1}, and a broad singlet at δ 1.74 ($C=C-C\underline{H}_3$) confirmed its structure. This is obviously the product due to diaxial opening of the ring A as shown in Chart 2.

Hederagenin derivative (**3c**) (type **C**) which has *trans*-diequatorial configuration between OH and $-CH_2-OTs$ groups again afforded a seco-compound (**9**) (IR: 1715 cm^{-1}) as a sole product. The structure was confirmed by a peak at δ 3.60 (overlapped with $-C^{28}\underline{H}_2-OH$), two broad singlets at δ 4.70 and 4.90, and a broad singlet at δ 1.77 in the NMR spectrum of the corresponding alcohol (**10**). The oxetane formation from **3c** is highly improbable because of high strain in a *trans*-fused 6—4 ring system. For the formation of the A-seco-compound (**G**) from type **C** monotosylate the reaction had to proceed *via* boat conformation (**C'**) to adopt diaxial arrangement of the substituents. The experimental results suggest that the latter reaction is energetically more favoured than the oxetane formation.

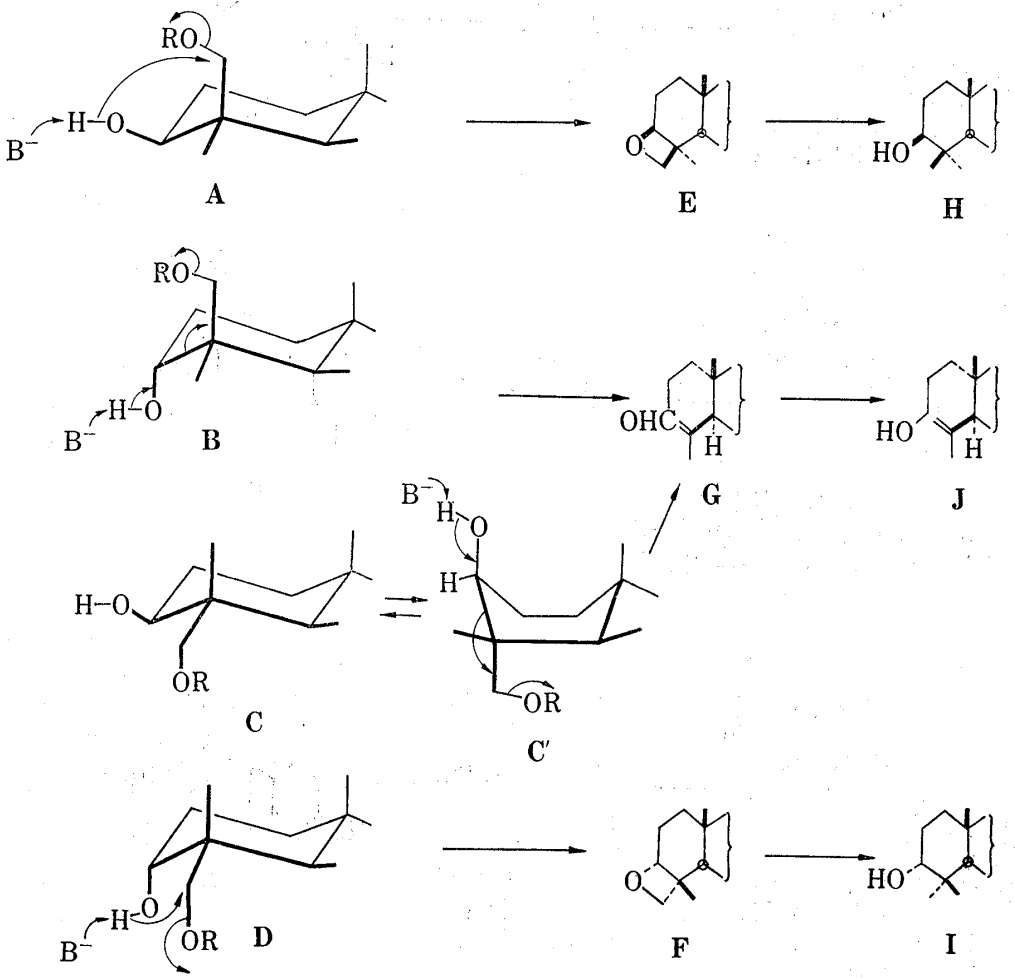


Chart 2

The results summarized in Chart 2 will be stated as follows; when 3-OH and 4-CH_2OTs are *cis* the product is an oxetane (**E** or **F**) and when they are *trans* the product is a seco-compound (**G**).[5] Since the formation of these compounds is stereospecific, we can adopt them as key-compounds to determine the relative stereochemistry of the diols **A**—**D**.

On lithium alminium hydrade (LAH) reduction the oxetanes, (**E**) and (**F**), slowly opened the ring at $-CH_2-O-$ linkage to give deoxy-compounds, (**H**) and (**I**), respectively. Thus, **5a** gave serratenediol (**11a**), and **6c** gave 3-epierythrodiol (**12**) in about 30—50% yield after 15—20 hr's reaction respectively, no other product except the starting material or a simiple reduction product (*i.e.*; **6b** from **6c**) being found in the reaction mixture.

LAH Reduction of 1,3-Glycol Monotosylates

When the monotosylates **A**—**D** were directly heated with LAH in tetrahydrofuran (THF) under reflux different reactions took place, and the reactions were complete within 3 hr in most cases. The results are listed in Table I. The reactions are classified into three types; i) oxetane or seco-compound formation, ii) sulfur-oxygen bond fission, and iii) alkyl-oxygen bond fission of tosylate.[6]

The first reaction is the same with that of *t*-butoxide, which obviously resulted from alkaline action of LAH, thus the product species again depend on the relative stereochemistry of –OH and $-CH_2OTs$ groups.

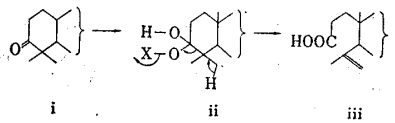
Table I. LAH Reduction of 1,3-Glycol Monotosylates

Monotosylates	Products			
	Oxetane (**E** or **F**)	A-Seco-alcohol (**G**)	C-O fiassion (**H** or **I**)	S-O fission (**A-D**)
A (1b)	40%	—	30%	30%
B (2b)	—	45%	—	55%
C (3c)	—	40%	35%	10%
D (4d)	—	—	100%	—
3-Deoxy comp. (**16b**)	—	—	—	>70%

Generally in hydride reduction of neopentyl or analogously hindered sulphonyloxy compound sulfur-oxygen bond fission occurs in preference to alkyl-oxygen fission. Thus reduction of **13** gave **14**,[7] and serratenediol monotosylate (**11c**) gave serratenediol (**11a**) as an only appreciable product. The glycols on the last column in Table I are the products of this sort. Remarkable distinction was that an appreciable formation of alkyl-oxygen fission product were observed in above reductions. Surprisingly direct reduction of mono-tosylate (**4c**) yielded a single product, 3-epierythrodiol (**12**) almost quantitatively.

One may assume that these deoxy-compounds (**H** and **I**) were produced by reductive cleavage of the intermediate oxetanes (**E** and **F**). This argument is, however, rejected from the fact that oxetanes were not reduced at all under similar conditions; for example **6c** was reduced to 3-epierythrodiol (**12**) only after 20 hr in about 40% yield.

5) For the source of natural A-seco-triterpenoid, the process (i)→(ii)→(iii) or its equivalent route has been proposed, since cleavage of (i) to dihydro- (iii) succeeded photochemically (D. Arigoni, D. H. R. Barton, R. Bernasconi, C. Djerassi, J.S. Mills, and R.E. Wolff, *J. Chem. Soc.*, **1960**, 1900). Our findings of high yield cleavage of 1,3-glycol monotosylate to an A-seco-aldehyde suggested an alternative possible source, pyrophosphate or sulfate of type **C** (or type **B**) glycol, which will easily be formed *in vivo* and be cleaved to an A-seco-aldehyde under solvolytic condition without light. Following oxidation (by air or by enzyme) gives a compound of dammalenolic acid type (iii).



i ii iii

6) These reactions are obviously competitive. Therefore, the ratio (i)/(ii)+(iii) changes depending upon the quality of LAH used for reduction.

7) A.S. Hussey, H.P. Liao, and R.H. Baker, *J. Am. Chem. Soc.*, **75**, 4727 (1953).

Another distinction in reductions between oxetane and monotosylate is the formation of an appreciable amount of erythrodiol (**15**) from the monotosylate (**3c**) of type **C** which can not form an oxetane.

These evidences imply the participation of C_3–OH for reductive removal of tosyloxy group. Presence of this neighbouring group participation was ascertained by the reduction of 3-deoxy-compound (**16b**) (for preparation of this compound—see Experimental). This compound slowly yielded the sulfur-oxygen fission compound (**17**) as a sole product, no 23-deoxy-compound being produced.

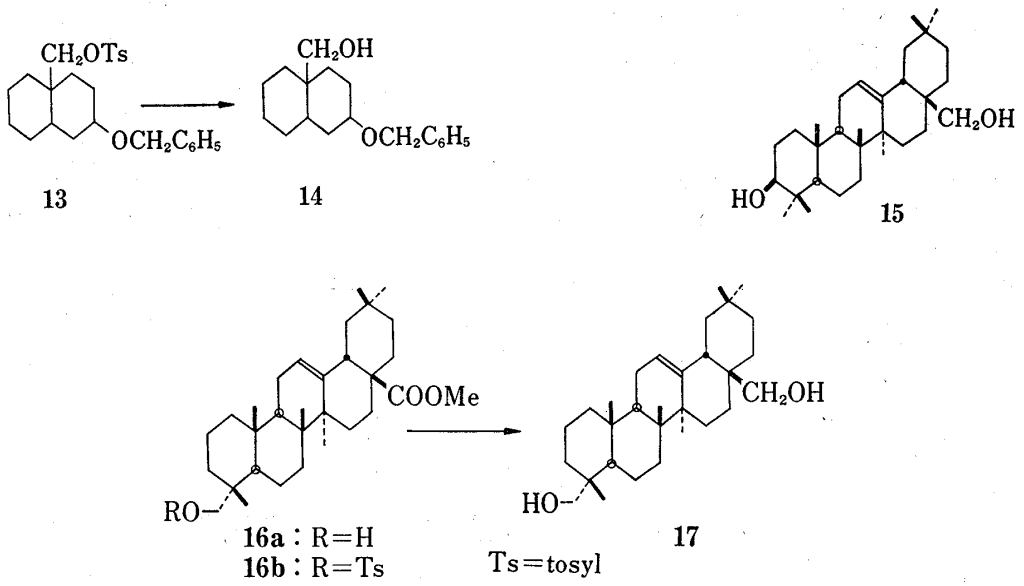


Chart 3

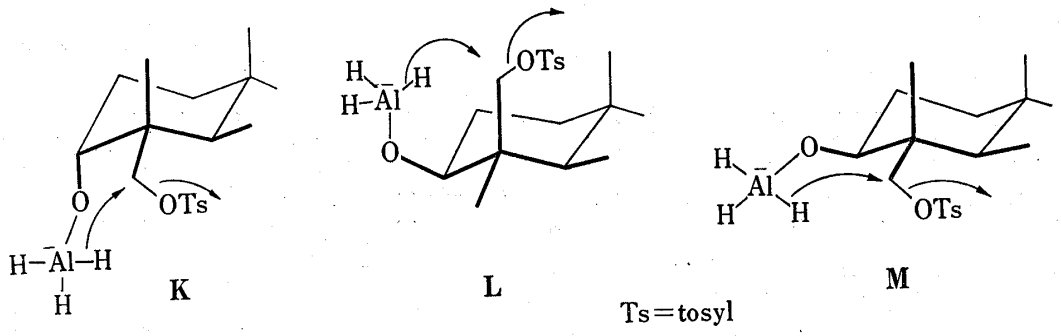


Chart 4

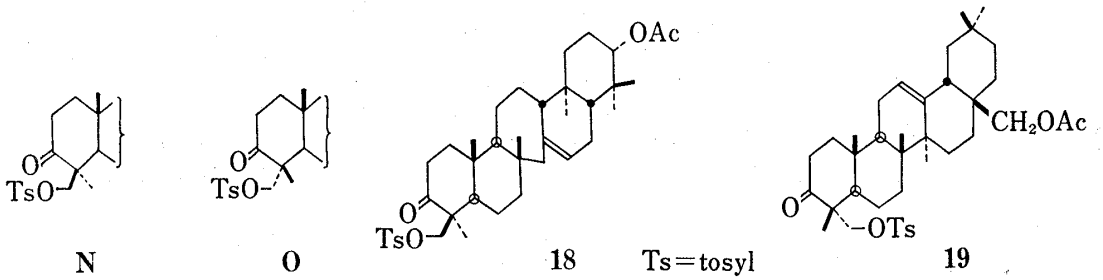
We therefore conclude that displacement of tosyloxy group by hydrogen in these 1,3-glycol monotosylates proceeds by intramolecular hydride transfer of such intermediate as depicted in (**K**)—(**M**). Similar cyclic transition state has been proposed in reductive ring opening of epoxy-alcohols.[8]

Lycoclavanol monotosylate (type **B**) can not form such a cyclic intermediate unless the ring were converted to boat form. Actually it gave the seco-alcohol (**8**) and lycoclavanol (**2a**) (S-O fission product); alkyl-oxygen fission did not occur to any noticeable extent.

LAH Reduction of the Keto-tosylates

The monotosylates **A**—**D** were smoothly oxidized by Jones' reagent to the keto-tosylates of two types, (**N**) and (**O**). The former showed positive and the latter did negative Cotton effects.[9]

8) H.B. Henbest and R.A.L. Wilson, *J. Chem. Soc.*, **1957**, 1958.
9) This fact can be used for determining stereochemistry of 4-CH_2OTs (thus of $-CH_2OH$) group.



N O 18 Ts=tosyl 19

Chart 5

LAH reduction of these keto-tosylates were essentially the same with that of the monotosylates **A** and **C**. Thus the keto-tosylates (**18**) (type **N**) gave the oxetane (**5a**), serratriol (**1a**; OH instead of OAc), and serratenediol (**11a**), and **19** (type **O**) gave the seco-compound (**10**), the triol (**3a**), and erythrodiol (**15**). The results indicate that the hydride firstly reduces the 3-keto group to 3β-alcohol. The formation of oxetane or seco-compound is again the key to distinguish the configuration of $-CH_2OTs$ group; the compound with 4β-CH_2OTs (**N**) gave an oxetane (**E**) while the compound with 4α-CH_2OTs (**O**) gave a seco-compound (**J**).

This procedure provides a method (**B**→**N**→**I**) to remove reductively the tosyloxy function from a glycol monotosylate of type **B** which otherwise cannot be reduced to the deoxy-compound (**I**).

Practical application of these reactions to structural and stereochemical problems will be reported in subsequent papers.

Experimental

Unless otherwise stated IR spectra were taken in Nujol mull. NMR spectra were measured in $CDCl_3$-using a 60 MHz machine, and melting point's were determined on a Yanagimoto melting point apparatus. Alumina used for chromatography was washed with 2.5% AcOH and reactivated. Identities were confirmed by IR and thin-layer chromatography (TLC) comparisons and by mixed fusion with respective authentic samples.

Transformation of Serratriol 24-Monotosylate[4] (1b) to the Oxetane (5b) by Chromatography——Serratriol 21-monoacetate[4] (**1a**; 1.76 g) and *p*-TsCl (4.00 g) in pyridine (50 ml) were kept for overnight. The crude product dissolved in benzene was loaded on alumina which was kept for 2 days, then eluated with the same solvent. i) First eluate gave 21-acetoxy-3β,24-ditosyloxy-serrat-14-ene,[4] mp 185—186°. ii) Second eluate gave a mixture (300 mg) which was further chromatographed in benzene over aliumina. Elution with benzene gave the oxetane **5b** (60 mg), mp 273—275°. iii) Third eluate gave the monotosylate **1b**[4] (370 mg), mp 188—189°, (needles from MeOH).

Lycoclavanol-24-tosylate (2b)——Lycoclavanol **2a** (110 mg) and *p*-TsCl (250 mg) in pyridine (10 ml) were kept for 5 hr at room temp. The mixture was poured into water and extracted with $CHCl_3$. The extract was washed with 5% HCl, water, and dried over $MgSO_4$, then evaporated. The residue was chromatographed in benzene over alumina. Elution with benzene and crystallization of benzene eluate (75 mg) from $CHCl_3$–MeOH gave **2b** as needles, mp 188—189.5°. IR: 3600, 3400 cm^{-1}. NMR: δ 0.69 (6H), 0.80 (3H), 0.90 (3H), 0.95 (3H), 1.03 (3H), 2.49 (3H), 3.49 (1H, b.s.), 3.68 (1H, b.s.), 3.99 (2H, ABq. J=10, δ_{AB}=21 Hz), 5.33 (1H, m.), 7.58 (4H, ABq. J=8, δ_{AB}=27 Hz). *Anal.* Calcd. for $C_{37}H_{56}O_5S$: C, 72.50; H, 9.21. Found: C, 72.31; H, 9.02.

28-Acetoxy-3β,23-dihydroxyoleanene (3b)——The compound **3b** (3 g) was obtained by hydrolysis of the corresponding acetonide[1] (3.5 g) with AcOH (20 ml)–$CHCl_3$ (60 ml)–water (10 ml) under reflux for 3 hr. It formed needles from *n*-hexane–ether and had mp 184—185°. IR: 3375, 1715, 1735 cm^{-1}; and 3430, 1718 cm^{-1} in $CHCl_3$. NMR: δ 0.89 (9H), 0.96 (3H), 0.98 (3H), 1.17 (3H), 2.05 (3H), 2.87 (2H, b.s.), 3.50 (1H, m.), 3.87 (2H, ABq. J=10, δ_{AB}=22 Hz), 5.20 (1H, m).

28-Acetoxy-3β-hydroxy-23-tosyloxyoleanene (3c)——The diol **3b** (1.2 g) and *p*-TsCl (900 mg) in pyridine (20 ml) were kept for 6 hr. at room temp. On working up, the monotosylate **3c** (284 mg) was obtained as needles. mp 201—202°. IR: 3540, 1726 cm^{-1}. NMR: δ 0.68 (3H), 0.98—0.91 (12H), 1.15 (3H), 2.06 (3H), 2.47 (3H), 3.87 (2H, ABq. J=12, δ_{AB}=22 Hz), 3.87 (2H, ABq. J=9, δ_{AB}=18 Hz), 5.20 (1H, m.), 7.58 (4H, ABq. J=8, δ_{AB}=27 Hz). *Anal.* Calcd. for $C_{39}H_{58}O_6S$: C, 71.52; H, 8.91. Found: C, 71.35; H, 8.76.

Methyl 3-Epihederagenate Monotosylate (4c)——Methyl 3-epihederagenate[1] **4a** (150 mg) and *p*-TsCl (500 mg) in pyridine (20 ml) were kept for 36 hr at room temp. The mixture was poured into water and

extracted with ether. The ethereal extract was washed with 5% HCl, water, dried over $MgSO_4$ and evaporated to give **4c** as an oil. IR(film): 3550, 1720, 1601 cm^{-1}. NMR: δ 0.70 (3H), 0.91 (12H), 1.12 (3H), 2.46 (3H), 3.63 (3H), 4.00 (2H, ABq. $J=9$, $\delta_{AB}=16$ Hz), 5.31 (1H, m), 7.62 (4H, ABq. $J=8$, $\delta_{AB}=28$ Hz).

28-Acetoxy-3α,23-dihydroxyoleanene (4b)——The compound **4b** (120 mg) was obtained by hydrolysis of the corresponding acetonide[1] (150 mg) on heating with 50% AcOH (50 ml) for 1 hr. It formed needles from *n*-hexane–ether and had mp 196—197°. IR: 3300, 1745, 1225 cm^{-1}. NMR: δ 0.71 (3H), 0.88 (6H), 0.96 (6H), 1.20 (3H), 2.04 (3H), 3.44 (2H, b.s.), 3.66 (1H, b.s.), 3.87 (2H, ABq. $J=11$, $\delta_{AB}=23$ Hz), 5.22 (1H, m.).

Tosylation of the Compound 4b——The monoacetate **4b** (90 mg) and *p*-TsCl (100 mg) in pyridine (20 ml) were allowed to stand for 36 hr at room temp. The product was taken up in ether and worked up as above to afford **4d** as an oil, which showed single spot on TLC apparently different from the starting material.

Chromatography of this oil (**4d**) in benzene over alumina changed it into the oxetane **6c** (60 mg) (needles from MeOH), mp 177—180°. The change of compound was confirmed by TLC. IR: 1750, 1225 cm^{-1}. NMR: δ 0.82 (3H), 0.90 (6H), 1.02 (3H), 1.04 (3H), 1.21 (3H), 2.06 (3H), 3.91 (2H, ABq. $J=11$, $\delta_{AB}=22$ Hz), 4.12 (2H, ABq. $J=5$, $\delta_{AB}=26$ Hz), 4.71 (1H, b.s.), 5.30 (1H, m.).

Hydrolysis of **6c** (50 mg) in 5% KOH–MeOH gave the alcohol (**6b**) as needles, mp 222—225°. IR: 3450 cm^{-1}. NMR: δ 0.80 (3H), 0.90 (6H), 1.01 (3H), 1.04 (3H), 1.22 (3H), 3.43 (2H, ABq. $J=11$, $\delta_{AB}=22$ Hz), 4.13 (2H, ABq. $J=5$, $\delta_{AB}=26$ Hz), 4.71 (1H, b.s.), 5.31 (1H, m.).

Reaction of the Monotosylate 1b (Type A) with *t*-BuOK——The monotosylate **1b** (20 mg) and *t*-BuOK (100 mg) in benzene (10 ml) were stirred for 30 min at room temp. and the mixture was poured into ice-water, then extracted with $CHCl_3$. The organic extract was washed with water, dried over $MgSO_4$, and evaporated to give the oxetane[4] **5a** (14 mg), mp 273—275°.

Reaction of the Monotosylate 4c (Type D) with *t*-BuOK——The monotosylate **4c** (80 mg) and *t*-BuOK (20 mg) in benzene (10 ml) was allowed to stand for 5 min at room temp. The product taken up in ether was worked up as above to afford the oxetane **6a** (45 mg) as needles, mp 214—217°. IR: 1730 cm^{-1}. NMR: δ 0.80 (6H), 0.93 (6H), 1.02 (3H), 1.17 (3H), 3.67 (3H), 4.10 (2H, ABq. $J=5$, $\delta_{AB}=26$ Hz), 4.70 (1H, b.s.), 5.39 (1H, m.).

Reaction of the Monotosylate 4d (Type D) with *t*-BuOK——The monotosylate **4d** (40 mg) was treated with *t*-BuOK (10 mg) in benzene (5 ml) for 3 min at room temp. On working up as above, the oxetane **6c** (25 mg), mp 177—180°, was isolated.

Reaction of the Monotosylate 2b (Type B) with *t*-BuOK——The monotosylate **2b** (35 mg) and *t*-BuOK (500 mg) in benzene (10 ml) was stirred for 1 hr at room temp. MeOH (15 ml) and $NaBH_4$ (50 mg) were added to the mixture which was stirred for further 1.5 hr, diluted with water, and extracted with $CHCl_3$. The extract was washed with water, dried over $MgSO_4$, and evaporated to give a seco-diol **8** (23 mg) as an oil which was purified by preparative TLC. IR($CHCl_3$): 3700, 3450, 892 cm^{-1}. NMR: δ 0.71 (3H), 0.81 (3H), 0.90 (6H), 0.96 (3H), 1.74 (3H), 3.51 (1H, b.s.), 3.63 (2H, t, $J=6$ Hz), 4.71 (1H, b.s.), 4.88 (1H, b.s.), 5.40 (1H, m.).

Reaction of the Monotosylate 3c (Type C) with *t*-BuOK——The monotosylate **3c** (86 mg) and *t*-BuOK (200 mg) in benzene (8 ml) were stirred for 1 hr at room temp. A small aliquot of this was acidified with dil. HCl and extracted with ether. The ethereal extract (**9**) after evaporation of the solvent showed IR ($CHCl_3$): 1715, 895 cm^{-1} and NMR: δ 9.30 (1H, s, –CHO). MeOH (10 ml) and $NaBH_4$ (200 mg) were added to the rest of the mixture which was stirred for further 1 hr, diluted with water, and extracted with $CHCl_3$. The crystalline residue obtained from $CHCl_3$ extract was purified by passing through alumina and crystallized from *n*-hexane–ether to afford the seco-diol **10** (50 mg) as needles, mp 205—207°. IR: 3300, 892 cm^{-1}. NMR: δ 0.90 (6H), 0.92 (3H), 1.00 (3H), 1.19 (3H), 1.77 (3H), 3.41 (2H, ABq. $J=11$, $\delta_{AB}=23$ Hz), 3.60 (2H, t, $J=6$ Hz), 4.70 (1H, b.s.), 4.90 (1H, b.s.), 5.25 (1H, m.). *Anal.* Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 80.82; H, 10.98.

LAH Reduction of the Monotosylate 1b (Type A)——The reaction (2 hr) as reported in ref. 4) afforded the oxetane (**5a**) (40%), serratenediol (**11a**) (30%), and serratriol (**1a**; OH instead of OAc) (30%).

LAH Reduction of the Monotosylate 2b (Type B)——The monotosylate **2b** (100 mg) and LAH (300 mg) in THF (30 ml) were heated under reflux for 1 hr. After addition of a few drops of water, the precipitate was filltered and washed with $CHCl_3$. The combined filtrate was dried over $MgSO_4$, and evaporated to give a residue which showed two spots on TLC. Separation with preparative TLC gave the seco-diol **8** (30 mg) (oil). The other product was lycoclavanol (**2a**; 40 mg), identified as its triacetate, mp 197—199°.

LAH Reduction of the Monotosylate 3c (Type C)——The monotosylate **3c** (230 mg) and LAH (500 mg) in THF (40 ml) were heated under reflux for 3.5 hr. On working up as above, the product gave three spots on TLC, which was separated by chromatography over alumina. i) Elution with benzene–CH_2Cl_2 (1 : 1) gave on oil which was again separated by preparative TLC to the seco-diol **10** (64 mg) (oil), and erythrodiol (**15**; 56 mg) (needles from $CHCl_3$–MeOH), mp 239—242°, (lit.[10] mp 232°) identical with specimen (mp 239—242°) obtained by LAH reduction of methyl oleanolate. ii) Futher elution with CH_2Cl_2–MeOH gave **3a** (17 mg), mp 261—263°.

10) J. Simonsen and W.C.J. Ross, "The Terpenes," Vol. IV, Cambridge Univ. Press., 1957 p. 245.

LAH Reduction of the Monotosylate 4c (Type D)——The monotosylate **4c** (120 mg) and LAH (300 mg) in THF (30 ml) were heated under reflux for 1 hr. On working up, 3-epierythrodiol (**12**; 80 mg) was obtained as an oil. NMR: δ 0.88 (9H), 0.95 (9H), 1.20 (3H), 3.41 (2H, ABq. $J=11$, $\delta_{AB}=23$ Hz), 3.45 (1H, diffused t. $J=3$ Hz), 5.25 (1H, m).

LAH Reduction of the Oxetane 5a——The oxetane **5a** (100 mg) and LAH (300 mg) in THF (30 ml) were heated under reflux for 16 hr. The product showed two spots on TLC which were separated by chromatography over alumina to give the starting material (70 mg) and serratenediol (**11a**; 15 mg).

LAH Reduction of the Oxetane 6c——i) The oxetane **6c** (35 mg) and LAH (100 mg) in THF (20 ml) were heated under reflux for 5 hr. The product showed single spot on TLC corresponding to the oxetane (**6b**).

ii) The mixture was heated for further 15 hr. The product isolated showed two spots on TLC corresponding to the oxetane (**6b**) and 3-epierythrodiol (**12**) in ratio of 1 : 1.

3β-Acetoxy-21-tosyloxyserrat-14-ene (11c)——Serratenediol 3-acetate **11b** (500 mg) in pyridine (10 ml) was tosylated with *p*-TsCl (1.269 g) for 2 days. Crystallization of the product from MeOH afforded **11c**, mp 167°.

LAH Reduction of the Monotosylate 11c——The tosylate **11c** (50 mg) and LAH (100 mg) in THF (20 ml) were refluxed for 5 hr. The product was purified by preparative TLC to furnish serratenediol **11a** (10 mg), mp 300°.

Methyl 3-Deoxyhederagenate (16a)——3-Oxo-23-trityloxyoleanene-28-oic acid methyl ester[1] (500 mg), 1,2-dithiolethane (5 ml), and BF_3–etherate (0.1 ml) in $CHCl_3$ (5 ml) were kept for 4 hr at room temp. The mixture was poured into 5% K_2CO_3 and extracted with ether. The ethereal extract was washed with water, dried over K_2CO_3, evaporated to dryness to give a residue which was purified by passing through alumina in CH_2Cl_2 affording a colorless oil (550 mg). The NMR spectrum indicated introduction of ethylenethioacetal and removal of the trityl group. δ 0.71 (3H), 0.86—0.91 (9H), 1.00 (3H), 1.20 (3H), 3.30 (4H), 3.63 (3H), 3.30 (1H, d, $J=12$ Hz), 4.05 (1H, d, $J=12$ Hz), 5.31 (1H, m).

The above oil in dioxan (20 ml) was heated under reflux with Raney–Ni (2 g) for 4 hr. Removal of the solvent and the solid left **16a** as an oil. IR ($CHCl_3$): 3580, 1720 cm^{-1}: NMR. δ 0.80 (3H), 0.85 (3H), 0.91 (3H), 0.93 (3H), 0.98 (3H), 1.17 (3H), 3.23 (2H, b.s.), 3.68 (3H), 5.31 (1H, m.).

Methyl 23-Tosyloxyoleanen-28-oate (16b)——3-Deoxy-compound **16a** (80 mg) and *p*-TsCl (300 mg) in pyridine (15 ml) were kept for 48 hr at room temp. The product (**16b**) was crystallized from *n*-hexane as needles, mp 153—154°. IR: 1730 cm^{-1}. NMR: δ 0.74 (3H), 0.87 (3H), 0.93 (9H), 1.13 (3H), 2.48 (3H), 3.67 (3H), 3.75 (2H, b.s.), 5.40 (1H, m), 7.66 (4H, ABq. $J=8$, $\delta_{AB}=28$ Hz).

LAH Reduction of the Tosylate 16b——The tosylate **16b** (50 mg) and LAH (150 mg) in THF (40 ml) were heated under reflux for 12 hr. The product in CH_2Cl_2 was purified by passing through a short column of alumina to afford **17** (24 mg) (needles from ether), mp 203—205°. IR: 3300 cm^{-1}. NMR: δ 0.86 (3H), 0.89 (6H), 1.00 (6H), 1.20 (3H), 3.26 (2H, ABq. $J=10$, $\delta_{AB}=20$ Hz), 3.41 (2H, ABq. $J=10$, $\delta_{AB}=22$ Hz), 5.23 (1H, m).

21-Acetoxy-3-oxo-24-tosyloxyserrat-14-ene (18)——The monotosylate **1b** (230 mg) in acetone (40 ml), was oxidized with Jones' reagent (0.5 ml; prepared from 1.03 g of CrO_3 in 30 ml of water and 8.7 ml of H_2SO_4) at 0° for 5 min. The mixture was diluted with water, extracted with ether which was washed with water, dried over $MgSO_4$, and evaporated to dryness. Crystallization of the residue (220 mg) from acetone gave **18** as needles, mp 211—213°. IR: 1720, 1700 cm^{-1}. NMR: δ 0.68 (3H), 0.81 (3H), 0.84 (6H), 0.93 (3H), 1.08 (3H), 2.03 (3H), 2.45 (3H), 4.20 (2H, ABq. $J=10$, $\delta_{AB}=24$ Hz), 4.50 (1H, m), 5.33 (1H, m), 7.53 (4H, ABq. $J=8$, $\delta_{AB}=26$ Hz). *Anal.* Calcd. for $C_{39}H_{56}O_6S$: C, 71.74; H, 8.64. Found: C, 71.81; H, 8.49. CD: $\Delta\varepsilon=+0.85$ at 294 nm (in dioxan).

28-Acetoxy-3-oxo-23-tosyloxyoleanene (19)——The tosylate **3c** (57 mg) in acetone (15 ml) was oxidized with Jones' reagent as above. The product (55 mg) was chromatographed in benzene over alumina and crystallized from MeOH to give **19** as needles, mp 183—185°. IR: 1720, 1700 cm^{-1}. NMR: δ 0.93 (9H), 1.02 (3H), 1.07 (3H), 1.20 (3H), 2.06 (3H), 2.48 (3H), 3.89 (2H, ABq. $J=11$, $\delta_{AB}=22$ Hz), 3.97 (2H, ABq. $J=8$, $\delta_{AB}=15$ Hz), 5.25 (1H, m), 7.59 (4H, ABq. $J=8$, $\delta_{AB}=27$ Hz). *Anal.* Calcd. for $C_{39}H_{56}O_6S$: C, 71.74; H, 8.64. Found: C, 71.44; H, 8.45. CD: $\Delta\varepsilon=-10.2$ at 300 nm (in dioxan).

LAH Reduction of the Keto-tosylate 18——The compound **18** (110 mg) and LAH (320 mg) in THF (20 ml) were heated under reflux for 15 hr. The product isolated as usual, gave three spots on TLC, which were separated by preparative TLC to afford the oxetane **5a** (23 mg), mp 273—275°, serratenediol (**11a**; 20 mg), and serratriol (**1a**; OH instead of –OAc; 5 mg). Serratenediol and serratriol were identified by converting to the corresponding acetate, respectively.

LAH Reduction of the Keto-tosylate 19——The keto-tosylate **19** (63 mg) and LAH (150 mg) in THF (10 ml) were refluxed for 5 hr. The product was separated by preparative TLC. The seco-diol **10** (10 mg), erythrodiol (**15**; 8 mg), and the triol **3** (17 mg) were obtained.