Tetrahedron. Vol. 28, pp 907 to 921. Pergamon Press 1972. Printed in Great Britain

PHOTOCHEMICAL TRANSFORMATION LEADING TO EUPTELEOGENIN—I

INTRODUCTION OF EPOXY-LACTONE SYSTEM

I. KITAGAWA, K. KITAZAWA and I. YOSIOKA
Faculty of Pharmaceutical Sciences, Osaka University, Toneyama, Toyonaka, Osaka, Japan

(*Received in Japan* 22 *September* 1971; *Received in the UK for publication* 29 *October* 1971)

Abstract—Being interested in the photochemical reactions which are potentially applied in the biogenetic-type chemical derivations of natural products, the appropriate photochemical means have been sought to produce the 11α,12α-epoxy-13β,28-lactone moiety in the oleanane skeleton, which is one of the unique functions of eupteleogenin (**2**). Photooxidation of oleanolic acid (**6a**) in acidic medium has been undertaken and desired 11α,12α-epoxy-oleanolic lactone (**12a**) obtained. Erythrodiol (**8a**) has been submitted to photooxidation and the 11α,12α-epoxy-13β,28-oxide moiety (**24a**) introduced along with skeletal rearrangement affording the 11α,12α-epoxy-taraxerene derivative (**25a**). During photooxidation of **8a**, it has been noticed that 11ξ-hydroxy-olean-12-ene derivatives (**28**, **42**) are fairly labile, allowing the transformation of dihydropriverogenin A(**10a**) into the thermodynamically less favored isomer priverogenin B(**9**).

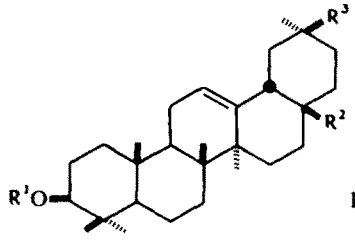
BIOGENETIC-TYPE SYNTHESIS[1] has been a subject of deep interest and an increasing number of works aiming at total syntheses of natural products with this conception have been presented in the recent literature.[2] On the other hand, a vast number of the photochemical reactions are being reported these days[3] and it is an attractive problem to devise photochemical reactions capable of transforming natural products[4] from one to another along the biogenetic-type paths.

We have been working on a biogenetic-type photochemical conversion of plant products and our attempts are presented in this and the following paper,[5] where our work on the oleanane type triterpenoids have eventually accomplished the transformation of spergulagenic acid (**1**) to eupteleogenin (**2**).

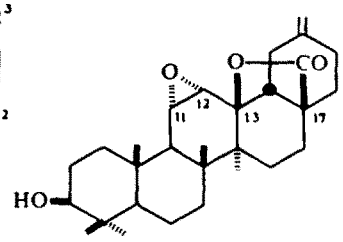
Eupteleogenin (**2**), a unique nor-triterpenoid characterized by an epoxy-lactone moiety and a terminal methylene function, was initially obtained from the antibiotic glycosides of the leaves of *Euptelea polyandra* Sieb. et Zucc. (*Eupteleaceae*) and its structure elucidated by Murata *et al.* on the basis of chemical evidence[6] and the X-ray analysis.[7] As one of the plausible biogenetic routes of eupteleogenin, we have assumed that introduction of these functions might occur at the later phase of biogenesis, for instance, after completion of the pentacyclic carbon skeleton.

At the same time, on the other hand, Corey *et al.*[8] presented a paper which dealt with the photooxidation of β-amyrin (**3**) resulting in the formation of 11α,12α-epoxy-taraxerol (**4**) and they showed a hydroperoxide (**5**) to be a possible intermediate during the photooxidative transformation.

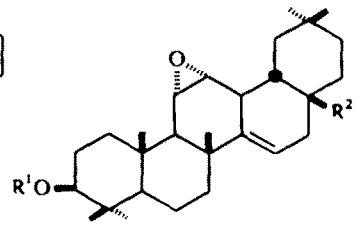
On this basis employing a compound possessing a carboxylic function at C-17 of the Δ^{12}-oleanene skeleton, e.g. oleanolic acid (**6a**), for the Corey's transformation, the 11α,12α-epoxy-13β,28-lactone moiety of eupteleogenin (**2**) would be introduced in a single step *via* a hypothetical intermediate (**7**) in which the carboxylic function



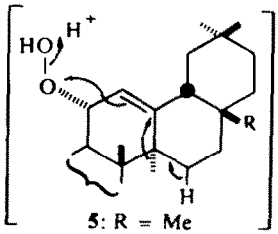
1: $R^1 = H$, $R^2 = R^3 = COOH$
spergulagenic acid
3: $R^1 = H$, $R^2 = R^3 = Me$
6a: $R^1 = H$, $R^2 = COOH$, $R^3 = Me$
b: $R^1 = Ac$, $R^2 = COOCH_3$, $R^3 = Me$
8a: $R^1 = H$, $R^2 = CH_2OH$, $R^3 = Me$
b: $R^1 = Ac$, $R^2 = CH_2OAc$, $R^3 = Me$



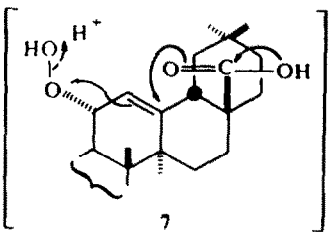
2: eupteleogenin



4: $R^1 = H$, $R^2 = Me$
25a: $R^1 = H$, $R^2 = CH_2OH$ (=E—2)
b: $R^1 = Ac$, $R^2 = CH_2OAc$

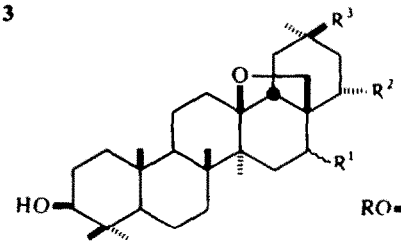


5: R = Me
26: R = CH_2OH

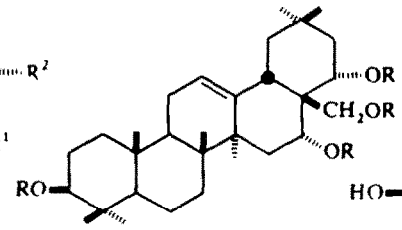


7

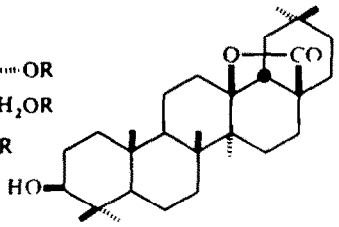
3



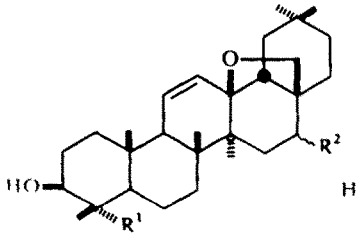
9: $R^1 = \alpha$—OH, $R^2 = OH$, $R^3 = Me$
priverogenin *B*
32: $R^1 = \alpha$—OH, $R^2 = H$, $R^3 = CHO$
33: $R^1 = \alpha$—OH, $R^2 = H$, $R^3 = Me$



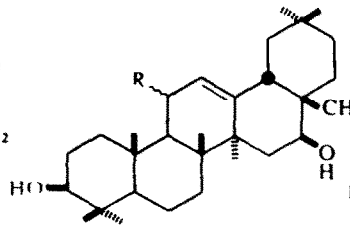
10a: R = H
dihydropriverogenin *A*
b: R = Ac



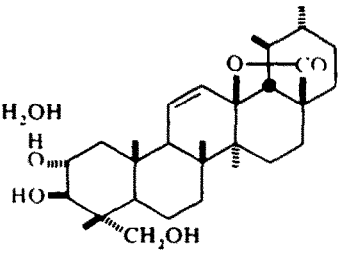
11



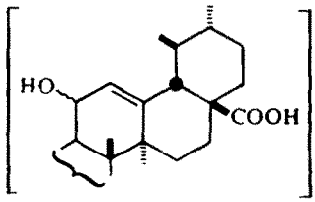
29: $R^1 = Me$, $R^2 = \beta$—OH
30: $R^1 = CH_2OH$, $R^2 = \beta$—OH
31: $R^1 = CH_2OH$, $R^H = \alpha$—OH



37a: R = H
b: R = OH



38



39

CHART *1*

at C-17 is participating. The assumption has been realized in the present paper. In addition, photooxidation of erythrodiol (**8a**) has been performed and as an extension of these studies, the partial synthesis of less stable priverogenin B (**9**)[9] from isomeric dihydropriverogenin A (**10a**)[9, 10] is also described.

Photooxidation of oleanolic acid[11]

Irradiation of the acidified ethanolic solution of oleanolic acid (**6a**) for 80 hr with occasional shaking to effect aeration afforded a crude product, whose TLC disclosed the formation of three products (designated as O–1, O–2, and O–3 from top to bottom on TLC) together with oleanolic lactone (**11**)* and unchanged starting material. Prep. TLC separation of the total mixture furnished O–1 (**12a**), O–2 (**13**), and O–3 (**14a**) with the respective yields of 8·5%, trace amount, and 10% and recovered oleanolic acid (26%).

The main product, O–3 (**14a**), was shown by elemental analysis and its mass spectrum to have molecular formula, $C_{30}H_{48}O_4$, (one more oxygen than that of oleanolic acid). The IR spectrum of O–3 shows the presence of OH (3530 cm^{-1}) and γ-lactone (1741 cm^{-1}) functions, while the NMR spectrum of O–3 exhibits a one-proton broad singlet ($W_{\frac{1}{2}}^{h}$ = 7 Hz) at 6·20 τ ascribable to a carbinyl proton geminal to an axial OH function along with signals due to seven C—Me function and a one-proton triplet-like signal at 6·87 τ characteristically assignable to C-3α-H. The NMR spectrum discloses a newly formed OH function in O–3, but lacks the signal due to the olefinic proton which was found in the starting material. These observations have led to the formulation of O–3 as 12α-hydroxy-oleanolic lactone (**14a**) and the presumption was verified by the direct comparison (m.m.p., TLC, and IR) of the monoacetyl derivative of O–3 with 3-O-acetyl-12α-hydroxy-oleanolic lactone (**14b**) which was prepared from 3-O-acetyl-oleanolic acid by Barton's procedure.[12]

The minor product, O–2 (**13**), was shown to possess an OH function by its IR absorption band at 3510 cm^{-1} but to lack the carbonyl function. Although it is assumed to be a decarboxylation product, further examination was not undertaken due to shortage of the material.

The second main product, O–1 (**12a**), possesses a molecular formula, $C_{30}H_{46}O_4$, of one more oxygen and two less hydrogens compared with oleanolic acid. The mass spectrum of O–1 exhibits the prominent fragment ion peaks at *m/e* 207 and *m/e* 189 ascribable to the ions (**i**) and (**ii**) derived through the reverse Diels-Alder type fragmentation,[13] which secure the preserved rings A and B of the starting compound in O–1. The IR spectrum of O–1 shows an absorption band of 870 cm^{-1} assignable to an epoxide ring[14] in addition to an OH (3536 cm^{-1}) and γ-lactone (1771 cm^{-1}) absorption bands. The presence of an epoxide ring in O–1 is further substantiated by a two-proton singlet at 7·05 τ ($W_{\frac{1}{2}}^{h}$ = 3 Hz) in the NMR spectrum, which is favorably comparable with the corresponding signal (2H singlet at 7·08 τ with $W_{\frac{1}{2}}^{h}$ = 3 Hz) of eupteleogenin (**2**).[6] The NMR spectrum also discloses the presence of seven C—Me functions and C-3α-H by a one-proton triplet-like signal at 6·82 τ. The accumulated physical data have led us to assume the aimed structure (**12a**) for O–1. It is noteworthy that the two protons on the epoxide ring are observed as a two-proton singlet in **12a** as in **2**, since the pattern is distinct from that reported in the previous papers.[15a, c]

Correctness of **12a** for O–1 was shown by the following derivatives. Treatment of

* Not isolated, but detected only on TLC by comparing with the authentic sample.

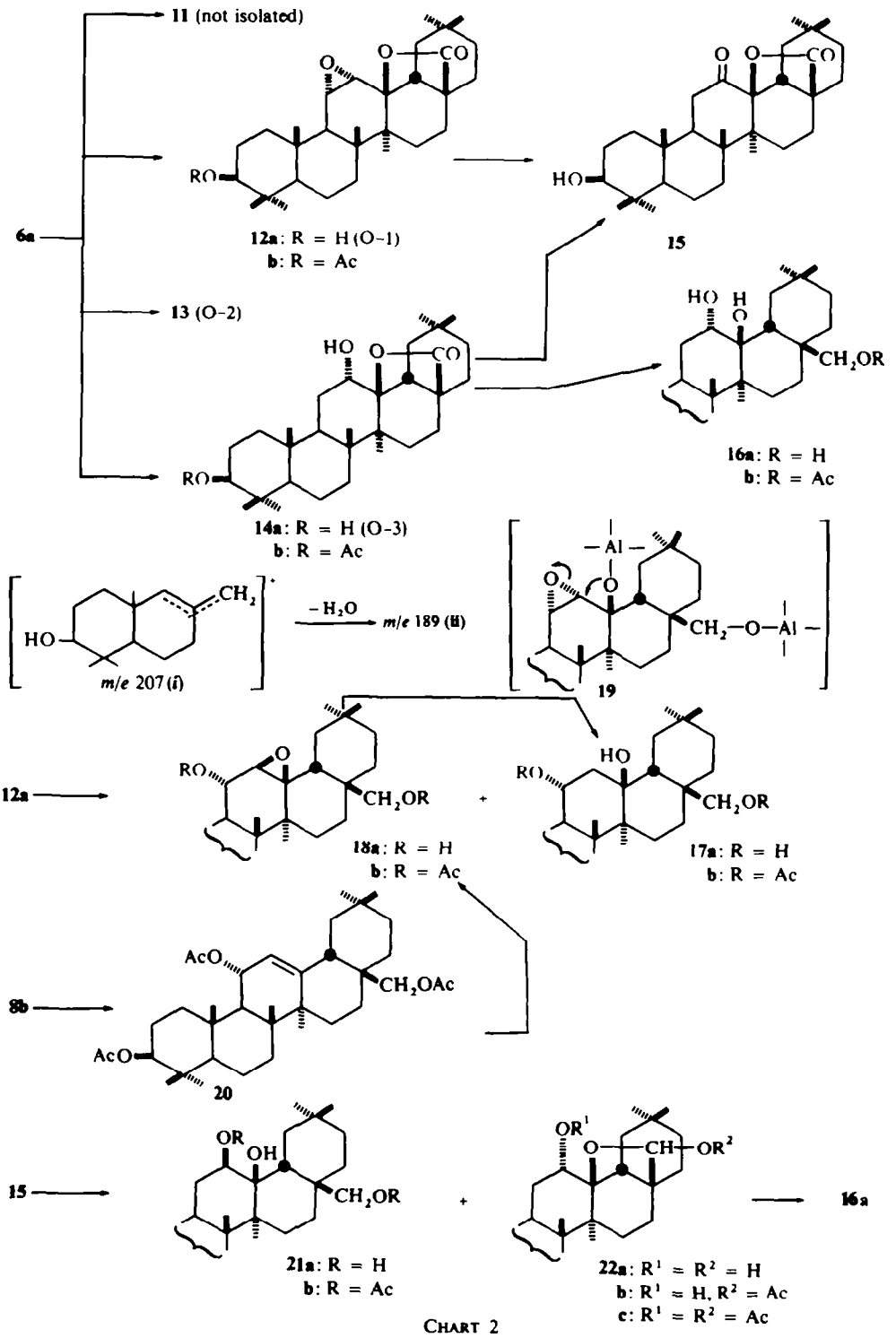

11 (not isolated)
6a
12a: R = H (O-1)
b: R = Ac
13 (O-2)
14a: R = H (O-3)
b: R = Ac
15
16a: R = H
b: R = Ac
m/e 207 (i)
-H2O
m/e 189 (ii)
19
12a
18a: R = H
b: R = Ac
17a: R = H
b: R = Ac
8b
20
15
21a: R = H
b: R = Ac
22a: R1 = R2 = H
b: R1 = H, R2 = Ac
c: R1 = R2 = Ac
16a

CHART 2

O-1 with ethanolic H_HSO_4 afforded 12-keto-oleanolic lactone (**15**), which was unambiguously procured from **14b** by CrO_3 oxidation followed by deacetylation. It follows therefore that introduction of a unique epoxy-lactone function has now been achieved in a single step starting from the ordinary Δ^{12}-17β-COOH moiety.[11]

Next, our attention was focused on the chemical behavior of the epoxy-lactone (**12a**). In general, it has been approved that an epoxide ring is opened by LAH reduction in a *trans*-diaxial manner and the epoxy-lactone (**12a**) is expected to afford a 12α-hydroxy derivative (**16a**), which is readily obtainable from **14a** by reduction using the same reagent. However, none of two reduction products of **12a** was found to be identical with **16a**. The minor product (**17a**) was shown to possess a newly formed equatorial OH function through ring opening of the epoxide moiety since it was readily acetylated to give a triacetate (**17b**) whose NMR spectrum (Table 1) exhibits a multiplet with broad half-band width (20 Hz)[15b] at 4·50 τ. The tetraol (**17a**) is formally equivalent to a reduction product formed *via* an equatorial ring opening of the epoxide ring.* The major reduction product is assigned **18a**. The NMR spectrum of the triacetate (**18b**) exhibits a one-proton doublet at 7·46 τ due to C-12α-H and a one-proton double doublet at 4·78 τ assignable to C-11β-H, and the small

TABLE 1*

	16b	**17b**	**18b**
	Me × 7 AcO × 2	Me × 7 AcO × 3	Me × 7 AcO × 3
$-C_{(28)}H_2OAc$	5·76, 5·56 (2H, ABq, 11)	5·72 (2H, s)	6·10, 5·69 (2H, ABq, 11)
$>C_{(12)}H-O-$	6·37 $\left(\text{1H, br.s, } W\frac{h}{2} = 7\right)$	—	7·46 (1H, d, 0·9)
$>C_{(11)}HOAc$	—	4·50 $\left(\text{1H, m, } W\frac{h}{2} = 20\right)$	4·78 (1H, d.d, 7·7 and 0·9)
$>C_{(3)}HOAc$	5·51 (1H, t-like)	5·56 (1H, t-like)	5·58 (1H, t-like)

* Measured at 60 MHz. The coupling constant (*J* value) and half-band width $\left(W\frac{h}{2}\right)$ in the parentheses in all Tables are given in Hz.

coupling constant (0·9 Hz) between both signals was confirmed by the decoupling experiment. Further reduction of **18a** with LAH gave **17a**, which also supports the formulation of **18a**.

As for the formation process of **18a**, the following consideration would be attractive. An oxygen function at C-13β in a probable intermediate (**19**) produced by initial reductive opening of the lactone moiety would have attacked the 12β side of the 11α,12α-epoxide ring to result in the formation of **18a**, that is, in a manner of the epoxide migration.[16] In order to achieve conclusive evidence on the structure, **18b** was prepared unambiguously from erythrodiol diacetate (**8b**). Thus, treatment of

* The tetraol **17a** is in fact considered to be a secondary product derived from **18a** as disclosed later.

8b with NBS/$Pb(OAc)_4$ in dry C_6H_6 afforded a triacetate (**20**), which possesses an 11α-acetoxyl function.[17] The triacetate (**20**) in turn was subjected to epoxidation using *m*-chloroperbenzoic acid[18] to give an epoxy-acetate identical with **18b** in all respects.

In connection with the fact that the 11α,12α-epoxy-13β,28-oxide moiety (**24a**) is unaffected by LAH reduction under the same reaction conditions as for **12a** (*vide infra*), it has been presumed that the probable intermediate (**19**) would be an inevitable step to cause the epoxide ring opening of **12a** under the condition employed. The driving force for the epoxide migration could be the formation of the more favored 12,13-epoxide structure (as in **18a**) as compared with the 11,12-epoxide (as in **12a** or **19**) since the former is comparable to the more favored Δ^{12}-oleanene while the latter to less favored Δ^{11}-oleanene.

For comparison purposes, reduction of **15** was pursued similarly as for **12a**. In this case, the 12β-hydroxy derivative (**21a**) was found to have the lactone ring reductively opened, whereas in the 12α-hydroxy product (**22a**) the lactone ring was reduced only up to a lactol moiety as revealed by NMR examination of the acetyl derivatives (**21b**, **22b**, and **22c**) (Table II). On further reduction with LAH, the lactol derivatives (**22b** + **22c**) furnished **16a**.

TABLE II*

	21b	**22b**	**22c**
	Me × 7	Me × 7	Me × 7
	AcO × 3	AcO × 2	AcO × 3
$-C_{(28)}\underline{H}_{(a)}-$	5·88, 5·39 (2H, ABq, 11)	4·05 (1H, s)	4·04 (1H, s)
$>C_{(12)}\underline{H}OR$	4·99 (1H, t-like)	6·21 $\left(1H, \text{br.s}, W\frac{h}{2} = 7\right)$	5·19 $\left(1H, \text{br.s}, W\frac{h}{2} = 7\right)$
$>C_{(3)}\underline{H}Ac$	*ca.* 5·5** (1H)	5·52 (1H, t-like)	5·52 (1H, t-like)

* Measured at 60 MHz.

** Coupling pattern is unclear due to the overlapping by the signals of $-C_{(28)}\underline{H}_2OAc$.

Photooxidation of erythrodiol[19]

On photooxidation of erythrodiol (**8a**), which possesses a 17β-CH_2OH function in place of 17β-COOH found in oleanolic acid (**6a**), participation of the unshared electron pair of 17β-CH_2OH is anticipated (*via* **23**) and formation of the 11α,12α-epoxy-13β,28-oxide moiety (as in **24a**) is expected. Since several oleanane sapogenins having the 13β,28-oxide function have been elucidated recently, introduction of the oxide function starting from Δ^{12}-17β-CH_2OH seems to be of interest.

Irradiation of erythrodiol for 100 hr as for oleanolic acid followed by prep. TLC separation afforded two products, designated as E-1 (5·8%) and E-2 (5·4%), in addition to the recovered starting material (13·2%).

The IR spectrum of E-1 (**24a**) shows the presence of an epoxide ring (870 cm^{-1})[14] together with the OH absorption band at 3580 cm^{-1}, whereas the NMR spectrum

of E-1 (Table III) offers evidences of the 11α,12α-epoxide ring by a two-proton singlet at 7·12 τ ($W_{\frac{1}{2}}^{h}$ = 3 Hz) assignable to C-11β-H and C-12β-H and of the 13β,28-oxide ring by a two-proton AB quartet at 6·73 and 6·30 τ (1H each, J = 6 Hz) due to the methylene protons at C-28.[20] Furthermore, the NMR spectrum of the mono-acetate (**24b**) (IR: 1725 and 1240 cm^{-1}) obtained readily from E-1 with Ac_2O and pyridine also satisfies the assignment (Table III). Therefore, the welcomed structure (**24a**) presumably derived through **23** has been promoted for E-1. The assignment was further corroborated by the quantitative conversion of **24b** to **12b** by RuO_4 oxidation.[21]

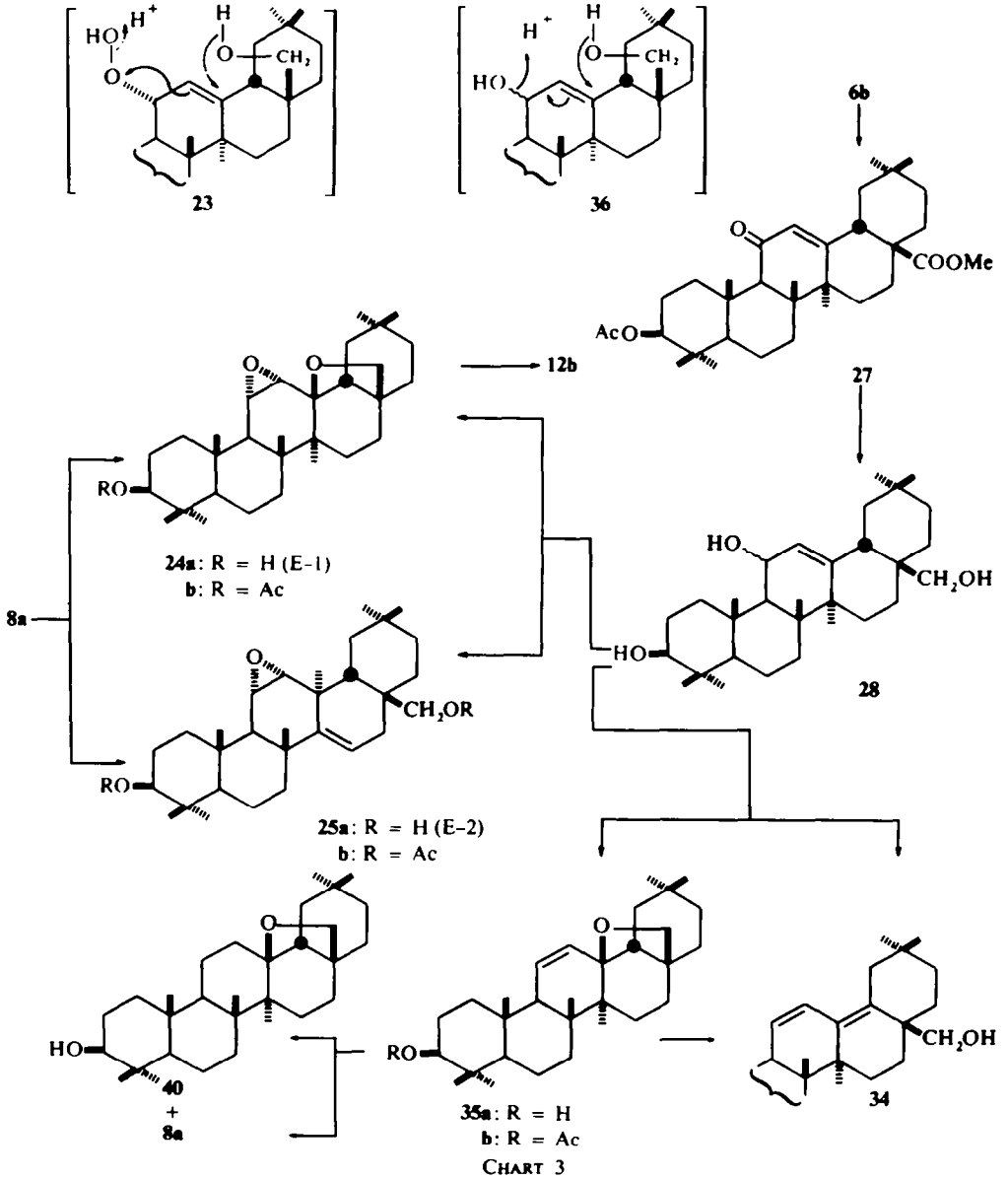


CHART 3

The other product, E-2 (**25a**), was shown to possess an OH (3500 cm^{-1}), a double bond (1630 cm^{-1}), and an epoxide ring (870 cm^{-1}) (IR). Acetylation of E-2 with Ac_2O and pyridine gave a diacetate (**25b**), whose NMR spectrum (Table III) exhibits a one-proton doublet at 7·30 τ (J = 5 Hz) and a one-proton triplet at 6·98 τ (J = 5 Hz). These signals are assignable to two protons on the epoxide ring and the chemical shifts and the coupling pattern resemble those of the corresponding protons in 11α,12α-epoxy-taraxerol (**4**).[8] In addition, a one-proton multiplet at 4·62 τ due to an olefinic proton at C-15 and a two-proton singlet at 6·36 τ assigned to the methylene protons of 17β-CH_2OAc together with a one-proton triplet-like signal at 5·56 τ of C-3α-H are observed in the NMR spectrum of **25b**. Referring to the observation on **4**[8] and anticipating another probable intermediate (**26**), these physical data have led to the reasonable formulation of **25a** for E-2.

TABLE III*

	24a	**24b**	**25b**
	Me × 7	Me × 7 AcO × 1	Me × 7 AcO × 2
$-C_{(11)}(O)-C_{(12)}-$ H H	7·12 (2H, s, $W\frac{h}{2}=3$)	7·16 (2H, s, $W\frac{h}{2}=3$)	7·30 (1H, d, 5) 6·98 (1H, t, 5)
$-C_{(28)}H_2-O-$	6·73, 6·30 (2H, ABq, 6)	6·76, 6·32 (2H, ABq, 6)	6·36 (2H, s)
$>C_{(3)}HOR$	6·77 (1H, t-like)	5·56 (1H, t-like)	5·56 (1H, t-like)
$=C_{(15)}H-$	--	—	4·62 (1H, m)

* Measured at 100 MHz.

Since Corey *et al.*[8] succeeded in the synthesis of **4** from β-amyrin (**3**) through an alternate process other than photooxidation, we have also attempted the synthesis of **24a** and **25a** through a similar reaction path. Oxidation of methyl 3-O-acetyl-oleanolate (**6b**) with t-butyl chormate yielded an 11-keto compound (**27**), which was then submitted to LAH reduction to furnish a triol (**28**). The triol was quite unstable, so that without purification it was treated with H_2O_2-*p*-TsOH in t-BuOH-CH_2Cl_2[8] immediately to yield **24a** (40%) and **25a** (13%). The unstable property of the triol (**28**) has been utilized at a key step of the transformation of dihydropriverogenin A (**10a**) into priverogenin B (**9**) as described below.

Transformation of dihydropriverogenin A to priverogenin B[22]

Among the naturally occurring oleanane triterpenoids, several are known to have the Δ^{11}-13β,28-oxide structure and some possess the 13β,28-oxide moiety without Δ^{11}. Saikogenin E (**29**)[20b, c], F (**30**)[20c], and G (**31**)[20b, c] belong to the former, while the sapogenins of *Primulaceous* plants such as priverogenin B (**9**)[9], cyclamiretin A (**32**),[23] and protoprimulagenin A (**33**)[24] to the latter. All of them have been characterized as the genuine sapogenins and have been demonstrated to readily convert to the second-

ary sapogenins, for instance, during acid hydrolysis of the parent saponins. Therefore, the synthesis of these sapogenins is of considerable interest.

As mentioned above, we have noticed the intermediary triol (**28**) to be rather unstable. For instance, heating the triol in MeOH afforded a new compound accompanied by a small amount of the diene (**34**), the latter being disclosed by a characteristic heteroannular diene triplet with low intensity in the UV spectrum (λ max nm (ε): 244 (269), 253 (302), 262 (109)). Two recrystallizations of the total product (MeOH) furnished a pure compound (**35a**) which shows only end absorption in the UV spectrum. Acetylation of **35a** in the usual manner gave a monoacetate (**35b**). The NMR spectra of **35a** and **35b** (Table IV) are comparable with that of saikogenin E (**29**)[20b,c] thus supporting the respective formulations. Formation of **35a** from **28** appears to be initiated by a trace of acidic contamination in MeOH (*via* **36**)* since it was found that the triol (**28**) was fairly stable even in boiling MeOH treated with alkali beforehand. Under the stronger acidic conditions, **35a** affords the diene (**34**) as was observed in saikogenins. It follows that the simple reaction path to introduce the Δ^{11}-13β,28-oxide moiety has become available.[22] At the same time, Kubota and Hinoh[20] were also successful in the transformation of longispinogenin (**37a**) to saikogenin E (**29**) through an 11-hydroxy derivative (**37b**).

TABLE IV*

	35a	**35b**
$-C_{(28)}H_2-O-C_{(13)}-$	6·72, 6·32 (2H, ABq, 7)	6·74, 6·31 (2H, ABq, 7)
$-C_{(11)}H=C_{(12)}H-$	4·65** 4·17 (2H, ABq, 11)	4·66** 4·15 (2H, ABq, 11)
$>C_{(3)}HOR$	6·81 (1H, t-like)	5·50 (1H, t-like)

* Measured at 60 MHz.

** The signal is further split into a doublet with J = 3 Hz.

Based on these observations, even the sapogenins of the Δ^{11}-13β,28-oxide type which are regarded as the genuine forms would be suspected as if the secondary products presumably derived from the 11-hydroxy-Δ^{12}-17β-CH_2OH structure. A similar consideration has been paid by Cheung and Tökes[25] for 2α,3β,23-trihydroxy-urs-11-en-13β,28-olide (**38**) which was isolated from *Dryobalanops aromatica* resin. They assumed **38** to be formed secondarily from a precursor (**39**) during the isolation procedure.

In order to develop the simple process of the synthesis of the Δ^{11}-13β,28-oxide system, we have attempted the preparation of priverogenin B (**9**) starting from dihydropriverogenin A (**10a**).

It was shown by Kubota and Hinoh[20c] that on catalytic hydrogenation in AcOH using Adam's catalyst saikogenin E (**29**) suffers hydrogenolysis affording longispinogenin (**37a**). Therefore, in a search for the appropriate conditions for preferential hydrogenation of the double bond at C-11, **35a** was treated under the various

* MeOH used here showed a three-proton doublet at 6·64τ (J = 2·4 Hz) and a collapsed one-proton quartet at 5·16τ (J = 2·4 Hz) in the NMR spectrum at 60 MHz.

conditions (H_2: atmospheric pressure or 3 atm.; catalyst: PtO_2, 5% Pd-C or Raney Ni (W-7); solvent: AcOH, EtOH, dioxane, or EtOAc) and finally hydrogenation over Raney Ni in EtOH was found satisfactory. The oxide (**35a**) furnished the desired saturated 13β,28-oxide (**40**) and erythrodiol (**8a**) in a ratio of 3:2. The NMR spectrum of **40** supports the formulation (Table V).

TABLE V*

	40	**43b**
	Me × 7	Me × 7 AcO × 2
$-C_{(28)}H_2-O-C_{(13)}-$	6·73, 6·24 (2H, ABq, 7)	6·56 (2H, s)
$-C_{(11)}H=C_{(12)}H-$	—	4·62† 4·13 (2H, ABq, 10·6)
$>C_{(3)}HOR$	6·77 (1H, t-like)	5·50 (1H, t-like)
$>C_{(16)}HOH$	—	5·72 (1H, d, 5·1)
$>C_{(22)}HOAc$	—	5·03 (1H, q, 6)

* Measured at 60 MHz.
† The signal is further split with J = 2·6 Hz.

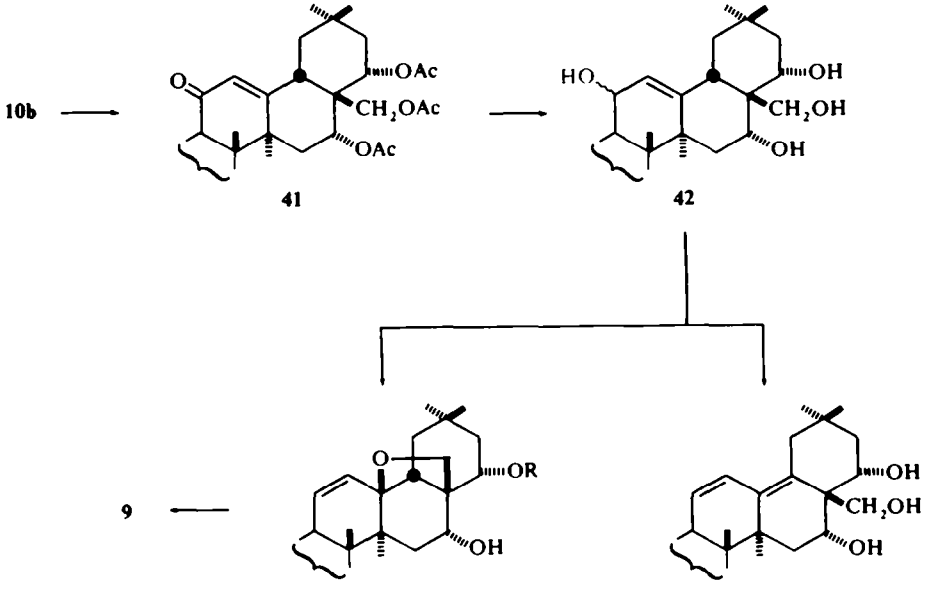


CHART 4

Next, the following transformation was undertaken. Oxidation of dihydropriverogenin A tetraacetate (**10b**) using t-butyl chromate gave an 11-keto derivative (**41**), which was then submitted to LAH reduction affording a pentaol (**42**). Without further purification, the pentaol was treated in MeOH under reflux thus giving the Δ^{11}-13β,28-oxide (**43a**) accompanied by a small amount of the diene (**44**). The NMR data of the diacetyl derivative (**43b**) substantiates the formulation (Table V). Finally, catalytic hydrogenation of **43a** over Raney Ni in EtOH afforded priverogenin B (**9**) in a good yield. The product due to hydrogenolysis (dihydropriverogenin A (**10a**)) was not detected in this case.

Taking advantage of the various information obtained here, the conversion of spergulagenic acid (**1**) into eupteleogenin (**2**) will be detailed in the following paper.[5]

EXPERIMENTAL

The following instruments were used for the physical data: m.p. (Yanagimoto Micro-meltingpoint Apparatus; Ishii High-meltingpoint Apparatus, a capillary type; recorded uncorrected); optical rotation (Rex Photoelectric Polarimeter, measured at room temperature with l = 1 dm and c = 1·0); IR spectra (Hitachi IR Spectrophotometer EPI-S2); UV spectra (Shimadzu UV Spectrophotometer MPS-50L); NMR spectra (Hitachi H-60 or Varian HA-100 NMR Spectrometer, in $CDCl_3$ and TMS as the internal standard). The chemical shifts are given in τ values and coupling constants (J) are in Hz. TLC, Silica gel D-5 (Camag) was used for TLC and detection by 1% Ce $(SO_4)_2$ in 10% H_2SO_4. For column chromatography, silica gel (Merck, 0·05–0·2 mm) was used.

Photooxidation of oleanolic acid (**6a**). A solution of **6a** (2 g) in 95% EtOH (400 ml, adjusted pH 2 by conc. HCl) was put into Pyrex tubes (1 × 20 cm) and irradiated externally with a 500 W high pressure mercury lamp (Eikosha Co, model PIH 500) at room temp for 80 hr. The tubes were 7 cm from the lamp and shaken occasionally. After evaporation of solvent, the product was subjected to prep. TLC developing with $CHCl_3$-MeOH-HCOOH (30 ml: 1 ml: a few drops) to give O–1 (**12a**, 8·5%), O–2 (**12**, trace), O–3 (**14a**, 10%) and recovered **6a** (26%).

A pure sample of 11α,12α-epoxy-oleanolic lactone (**12a**) (O–1), m.p. 269–271·5°, was obtained by recrystallization from MeOH as colorless needles; $[\alpha]_D$ + 21° ($CHCl_3$); ν_{max} (KBr): 3536, 1771, 870 cm^{-1}, NMR (100 MHz): 9·22 (3H), 9·09 (3H), 9·03 (6H), 9·00 (3H), 8·96 (3H), 8·92 (3H) (all s, totally seven Me's), 7·05 (2H, s, $W_{\frac{1}{2}}$ = 3 Hz), 6·82 (1H, t-like); Mass spectrum *m/e* (%): 470 (M^+, 4·1), 207 (**i**, 15), 189 (**ii**, 53·3), 95 (100) (Found: C, 76·33; H, 9·64. $C_{30}H_{46}O_4$ requires C, 76·55; H, 9·85%).

Acetylation of **12a** (10 mg) with Ac_2O (0·3 ml) and pyridine (0·5 ml) overnight at room temp afforded a product (9 mg), which was crystallized from MeOH giving 3-O-acetyl-11α,12α-epoxy-oleanolic lactone (**12b**) as colorless needles m.p. > 300°; $[\alpha]_D$ + 43° ($CHCl_3$); ν_{max} (KBr): 1772, 1725, 1240, 872 cm^{-1} (γ-lactone, acetate, epoxide) (Found: C, 75·02; H, 9·61. $C_{32}H_{48}O_5$ requires C, 74·96; H, 9·44%).

O–2 (**13**) was purified by recrystallization from MeOH to give colorless plates m.p. 251–255°; ν_{max} (KBr): 3510, 870 cm^{-D}.

Recrystallization from MeOH gave a pure sample of 12α-hydroxy-oleanolic lactone (**14a**) = O–3) as colorless plates, m.p. 274–278°; $[\alpha]_D$ + 67° ($CHCl_3$); ν_{max} (KBr): 3530, 1741 cm^{-1}; NMR (100 MHz): 9·24 (3H), 9·12 (6H), 9·04 (9H), 8·88 (3H) (all s, totally seven Me's), 6·84 (1H, t-like), 6·20 (1H, br.s, $W_{\frac{1}{2}}$ = 7 Hz) (Found: C, 76·13; H, 10·38. $C_{30}H_{48}O_4$ requires C, 76·22; H, 10·24%). Treatment of **14a** (30 mg) with Ac_2O (0·5 ml) and pyridine (1·5 ml) at room temp gave a product which was crystallized from MeOH and identified by m.m.p., IR, and TLC with authentic 3-O-acetyl-12α-hydroxy-oleanolic lactone (**14b**) prepared by Barton.[12]

Acid treatment of **12a** *giving* **15**. A solution of **12a** (17 mg) in 6N H_2SO_4 (3 ml)-EtOH (4 ml) mixture was refluxed for 40 min on a water-bath. After cooling the mixture was diluted with water, extracted with ether and treated as usual. Prep. TLC of the product with $CHCl_3$-acetone-EtOH (95:5:0.5) afforded a carbonyl compound (4 mg) which was recrystallized from MeOH and identified by m.m.p., IR, and TLC with authentic 12-keto-oleanolic lactone (**15**) prepared as below.

12-*Keto-oleanolic lactone* (**15**). To a stirred solution of **14b** (200 mg) in acetone (50 ml), was added dropwise CrO_3 (3 ml) (composition: CrO_3 2·66 g, conc. H_2SO_4 2·3 ml, water 7·7 ml) at room temp and the mixture was kept stirring for further 20 min and diluted with water. The white precipitate was collected

and dried to give 3-O-acetyl-12-keto-oleanolic lactone (173 mg). The acetate was then dissolved in 5% NaOH–MeOH (10 ml), refluxed for 10 min on a water-bath, diluted with water, and acidified with dil. H_2SO_4. The keto-lactone (**15**) obtained as a white precipitate was collected, dried, and crystallized from MeOH, m.p. 271–274°, (147 mg).

LAH reduction of 11α,12α-*epoxy-oleanolic lactone* (**12a**). To a solution of LAH (250 mg) in dry ether (30 ml), was added dropwise a solution of **12a** (120 mg) in dry THF (10 ml) and the total mixture refluxed for 3 hr. After cooling excess LAH was decomposed by addition of AcOEt and Na_2SO_4 aq. The mixture was added to Na_2SO_4 and the resulting clear organic layer was decanted. The residual inorganic portion was washed with ether and the combined organic layers washed with water, dried (Na_2SO_4), and evaporated to dryness to furnish a mixture (*ca.* 100 mg) of **17a** and **18a**. Acetylation with Ac_2O (3 ml) and pyridine (5 ml) in the usual manner gave a mixture of acetates (**17b** and **18b**), separated by prep. TLC developing with C_6H_6–$CHCl_3$ (1:3) to give **17b** (20 mg) and **18b** (65 mg).

Recrystallization from MeOH–CH_2Cl_2 gave pure 3β,11α,28-triacetoxy-13β-hydroxy-oleanane (**17b**), colorless plates, m.p. 264–267°; $[\alpha]_D$ + 24° ($CHCl_3$); ν_{max} ($CHCl_3$): 3500 (br), 1720 cm^{-1}; NMR (60 MHz): 9·17 (3H), 9·14 (9H), 9·00 (3H), 8·85 (3H), 8·75 (3H) (all s, totally seven Me's), 7·96, 7·94, 7·80 (3H each, all s, three AcO's), and the other signals as given in Table I (Found: C, 71·43; H, 10·05. $C_{36}H_{58}O_7$ requires C, 71·72; H, 9·70%).

A pure sample of 3β,11α,28-triacetoxy-12β,13β-epoxy-oleanane (**18b**) was obtained as colorless plates m.p. 270–273° by recrystallization with aq. MeOH; $[\alpha]_D$ + 39° ($CHCl_3$); ν_{max} (KBr): 1728, 1244 cm^{-1}; NMR (60 MHz): 9·20 (3H), 9·14 (6H), 9·06 (3H), 8·99 (3H), 8·85 (3H), 8·37 (3H) (all s, totally seven Me's), 7·93 (9H, s, three AcO's), and the other signals as given in Table I (Found: C, 71·66; H, 9·49. $C_{36}H_{58}O_7$ requires C, 71·96; H, 9·40%).

Reduction of **18b** with LAH in dioxane (reflux for 3 hr) furnished **17a** quantitatively. Neither unchanged **18b** nor **18a** was detected in the reaction product.

LAH reduction of 12α-*hydroxy-oleanolic lactone* (**14a**). To a solution of LAH (250mg) in dry dioxane (15 ml), was added dropwise a solution of **14a** (100 mg) in dry dioxane (10 ml). The mixture was then refluxed for 15 hr and treated similarly as for reduction of **12a**. Acetylation of the product (**16a**, 72 mg) with Ac_2O (2 ml) and pyridine (3 ml) gave a product (65 mg), crystallized from MeOH–CH_2Cl_2 to give 3β,28-diacetoxy-12α,13β-dihydroxy-oleanane (**16b**) colorless needles m.p. 198–201°; $[\alpha]_D$ + 43° ($CHCl_3$); ν_{max} (KBr): 3460, 1715 (br), 1250 (br) cm^{-1}; NMR (60 MHz): 9·14 (3H), 9·12 (6H), 9·09 (6H), 8·83 (3H), 8·72 (3H) (all s, totally seven Me's), 7·95 (3H), 7·93 (3H) (both s, two AcO's), and the other signals as given in Table I (Found: C, 72·99; H, 9·74. $C_{34}H_{56}O_6$ requires C, 72·82; H, 10·06%).

Acetoxylation of 3,28-*di-O-acetyl-erythrodiol* (**8b**). To a solution of **8b** (200 mg) in dry C_6H_6 (15 ml), were added NBS (120 mg) and $Pb(OAc)_4$ (200 mg) and the mixture refluxed for 30 min and treated in the usual manner to yield 11α-acetoxy-3,28-di-O-acetyl-erythrodiol (**20**) (130 mg, amorphous); $[\alpha]_D$ −16° ($CHCl_3$); ν_{max} ($CHCl_3$): 1735, 1242 cm^{-1}; NMR (60 MHz): 9·13 (12H), 8·98 (3H), 8·94 (3H), 8·73 (3H) (all s, totally seven Me's), 8·01 (3H), 7·96 (6H) (all s, three AcO's), 6·32, 6·00 (2H, ABq., J = 11, $-C_{(28)}\underline{H}_2OAc$), 5·53 (1H, t-like, $>C_{(3)}\underline{H}OAc$), 4·51–4·83 (2H, m, $>C_{(11)}\underline{H}OAc$ and $-C_{(12)}\underline{H}=$). (Found: C, 70·77; H, 9·60. $C_{36}H_{58}O_8 \cdot \frac{1}{2}H_2O$ requires C, 70·70; H, 9·66%).

Epoxidation of **20**. To a stirred solution of **20** (30 mg) in CH_2Cl_2 (5 ml), was added dropwise a solution of *m*-Cl-perbenzoic acid (35 mg) in CH_2Cl_2 (10 ml) and the mixture was stirred at 25° for 1 hr to yield a complex mixture (TLC). Prep. TLC separation developing with $CHCl_3$-acetone (30:1) afforded a pure product 3·1 mg) which was identified with **18b** by IR and TLC.

LAH reduction of 12-*keto-oleanolic lactone* (**15**). To a solution of LAH (300 mg) in dry ether (30 ml), was added dropwise a solution of **15** (200 mg) in dry THF (10 ml) and the mixture was refluxed for 3 hr and treated in the usual manner yielding a mixture (152 mg) of **21a** and **22a**. Acetylation with Ac_2O (3 ml) and pyridine (5 ml) (overnight at room temp) gave a mixture of the acetates (150 mg), which was subjected to prep. TLC to afford **21b** (48 mg) and **22b** (71 mg).

Analytical sample of 3β,12β,28-hydroxy-oleanane (**21b**) was obtained by recrystallization from MeOH, colorless needles, m.p. 219–221°; $[\alpha]_D$ + 38° ($CHCl_3$); ν_{max} ($CHCl_3$): 3550 (br), 1725, 1245 cm^{-1}; NMR (60 MHz): 9·20 (3H), 9·14 (6H), 9·10 (6H), 8·89 (3H), 8·82 (3H) (all s, totally seven Me's), 7·96 (6H), 7·92 (3H) both s, three AcO's), and the other signals as given in Table II (Found: C, 71·58; H, 9·78. $C_{36}H_{58}O_7$ requires C, 71·72; H, 9·70%).

Analytical sample of the lactol-diacetate (**22b**) was obtained by recrystallization from MeOH, colorless plates, m.p. 208–211°; $[\alpha]_D$ + 63° ($CHCl_3$); ν_{max} (KBr): 3440 (br), 1720, 1250 cm^{-1}; NMR (60 MHz): 9·14

(6H), 9·11 (3H), 9·08 (3H), 9·03 (3H), 8·79 (6H) (all s, totally seven Me's), 7·96, 7·94 (3H each s, two AcO's), and the other signals as given in Table II (Found: C, 72·94; H, 10·03. $C_{34}H_{54}O_6$ requires C, 73·08; H, 9·74%).

Acetylation of lactol-diacetate (**22b**). Acetylation of **22b** (50 mg) with Ac_2O (1 ml) and pyridine (2 ml) under reflux for 2 hr followed by the usual work up afforded a product (45 mg), which was crystallized from aq. MeOH to give the lactol-triacetate (**22c**) as colorless plates, m.p. 138–141·5°; $[\alpha]_D$ + 109° ($CHCl_3$); ν_{max} (KBr): 1735, 1240 cm^{-1}; NMR (60 MHz): 9·12 (12H), 9·03 (3H), 8·81 (3H), 8·78 (3H) (all s, totally seven Me's), 7·95 (3H), 7·91 (6H) (both s, three AcO's), and the other signals as given in Table II (Found: C, 71·90; H, 9·41. $C_{36}H_{56}O_7$ requires C, 71·96; H, 9·40%).

LAH reduction of the lactol acetates (**22b** + **c**) under the same reaction condition as for reduction of **14a** (dioxane, reflux for 15 hr) furnished **16a**.

Photooxidation of erythrodiol (**8a**). Irradiation of **8a** (2 g) in acidified 95% EtOH (400 ml) with occasional aeration for 100 hr under the same reaction conditions as for oleanolic acid (**6a**) afforded a mixture whose separation was effected by prep. TLC developing with $CHCl_3$—AcOEt (5:1) to give E-1 (**24a**, 5·8%), E-2 (**25a**, 5·4%), and recovered **8a** (13·2%). Recrystallization from MeOH afforded a pure sample of 3β-hydroxy-11α,12α;13β,28-diepoxy-oleanane (**24a**), colorless needles, m.p. 259–261°; $[\alpha]_D$ −42° (pyridine); ν_{max} (KBr): 3580, 870 cm^{-1}; NMR (100 MHz): 9·22 (3H), 9·08 (3H), 9·02 (12H), 8·94 (3H) (all s, totally seven Me's), and the other signals as given in Table III (Found: C, 78·58; H, 10·80. $C_{30}H_{48}O_3$ requires C, 78·89; 10·59%).

Analytical sample of 28-hydroxy-11α,12α-epoxy-taraxerol (**25a**) was obtained by recrystallization from MeOH as colorless needles, m.p. 268–271°; $[\alpha]_D$ −56° (pyridine); ν_{max} (KBr): 3500, 1630, 870 cm^{-1} (Found: C, 78·85; H, 10·61. $C_{30}H_{48}O_3$ requires C, 78·89; H, 10·59%).

Acetylation of **24a**. The diepoxide (**24a**, 50 mg) was acetylated with Ac_2O (0·5 ml) and pyridine (1 ml) and treated in the usual manner to give a product (50 mg), which was crystallized from MeOH to give 3β-acetoxy-11α,12α;13β,28-diepoxy-oleanane (**24b**) as colorless needles, m.p. 275–276°; $[\alpha]_D$ −36° ($CHCl_3$); ν_{max} (KBr): 1725, 1240, 870 cm^{-1}; NMR (100 MHz): 9·17 (6H), 9·11 (3H), 9·05 (6H), 9·00 (3H), 8·60 (3H) (all s, totally seven Me's), and the other signals as given in Table III (Found: C, 76·86; H, 10·04. $C_{32}H_{50}O_4$ requires C, 77·06; H, 10·11%).

Acetylation of **25a**. Treatment of **25a** (30 mg) with Ac_2O (0·5 ml) and pyridine (1 ml) as usual yielded a product (29 mg), which was crystallized from MeOH to give 28-acetoxy-11α,12α-epoxy-3-O-acetyl-taraxerol (**25b**) as colorless needles, m.p. 256–260°; $[\alpha]_D$ −51° ($CHCl_3$); ν_{max} (KBr): 1730, 1245, 1635, 870 cm^{-1}; NMR (100 MHz): 9·16 (6H), 9·13 (3H), 9·07 (3H), 9·01 (3H), 8·95 (3H), 8·93 (3H) (all s, totally seven Me's), 8·01 (6H, s, two AcO's), and the other signals as given in Table III (Found: C, 75·47; H, 9·56. $C_{34}H_{52}O_5$ requires C, 75·51; H, 9·69%).

RuO_4 *oxidation of* **24b**. RuO_4–CCl_4 solution: To an ice-cooled suspension of RuO_2 (200 mg) in CCl_4 (25 ml), was added aq. $NaIO_4$ solution ($NaIO_4$ 1·6 g and water 25 ml) and the mixture kept stirring under ice-cooling for one hr. The CCl_4 layer was taken, filtered to remove black precipitates and was added again with aq. $NaIO_4$ solution ($NaIO_4$ 0·5 g and water 25 ml) with stirring thus giving a yellow RuO_4–CCl_4 solution.

To a stirred solution of **24b** (49 mg) in CCl_4 (10 ml), was added dropwise at room temp the aforementioned RuO_4–CCl_4 solution (10 ml) and the total mixture stirred for further 2 hr. After addition of iso-PrOH to decompose excess RuO_4, the black precipitate (RuO_2) was removed by filtration. Evaporation of the solvent afforded a product a product (45 mg), which was crystallized from MeOH and identified with 3-O-acetyl-11α,12α-epoxy-oleanolic lactone (**12b**) by m.m.p., IR, and TLC.

Methyl 3-O-*acetyl*-11-*keto-oleanolate* (**27**). To a stirred warm solution of methyl 3-O-acetyl-oleanolate (**6b**) (5 g) in dry CCl_4 (80 ml), was added dropwise a mixture of t-butyl chromate-CCl_4 solution (80 ml),[H6] AcOH (30 ml), and Ac_2O (15 ml) and the mixture refluxed for 3 hr. After cooling, the mixture was treated with aq. oxalic acid and then with crystals of oxalic acid to decompose excess t-butyl chromate, and extracted with CCl_4. The organic layer was treated in the usual way and evaporated to dryness. Recrystallization of the product with MeOH gave **27** (4·1 g), m.p. 245–248° (colorless needles); ν_{max} ($CHCl_3$): 1718, 1250 (ester), 1649 (six-membered ring enone) cm^{-1}.

LAH reduction of **27**. To a solution of LAH (300 mg) in dry ether (25 ml), was added a solution of **27** (200 mg) in dry ether (10 ml) —C_6H_6 (10 ml), and the total was refluxed for 4 hr. After cooling, the mixture was treated with MeOH, aq. 10% NaOH, extracted with ether and worked up as usual. Since the product, 11ξ-hydroxy-erythrodiol (**28**) (160 mg) was fairly unstable, it was submitted to further reaction without purification.

H_2O_2-*p*-TsOH *oxidation of* **28**. To a stirred solution **28** (160 mg) in CH_2Cl_2 (20 ml), was added dropwise

a solution of t-BuOH (8 ml) containing *p*-TsOH (240 mg) and 30% H_2O_2 (1 ml) at room temp and the total mixture allowed to stand overnight with stirring. After diluting with water, the mixture was extracted with CH_2Cl_2 and the organic layer washed with water, aq. 5% $NaHCO_3$, and water successively and treated as usual to give a product (143 mg). Silica gel (13 g) column chromatography of the product furnished **24a** (68 mg) and **25a** (22 mg), both of which were identified by m.m.p., IR, and TLC with the compoupds above procured through photooxidation of erythrodiol (**8a**).

Treatment of **28** *with hot* MeOH. The triol (**28**, 200 mg) was dissolved in hot MeOH and the solution heated on a water-bath for a few min. After cooling, colorless needles (140 mg) separated out and were collected. Recrystallization twice afforded Δ^{11}-13β,28-oxide derivative (**35a**, 124 mg) as colorless needles, m.p. 225–226°; $[\alpha]_D$ + 115° ($CHCl_3$); ν_{max} ($CHCl_3$): 3440, 1645 cm^{-1}; NMR (60 MHz): 9·21 (3H), 9·11 (3H), 9·09 (3H), 9·02 (9H), 8·90 (3H) (all s, totally seven Me's), and the other signals as given in Table IV (Found: C, 81·62; H, 10·90. $C_{30}H_{48}O_2$ requires C, 81·76; H, 10·98%).

Acetylation of **35a**. The oxide (**35a**, 50 mg) was treated with Ac_2O (1 ml) and pyridine (2 ml) in the usual way to yield an acetate (48 mg), which was crystallized from MeOH to afford **35b** as colorless needles, m.p. 221–223°; $[\alpha]_D$ + 127° ($CHCl_3$); ν_{max} ($CHCl_3$): 1719, 1256 cm^{-1}; NMR (60 MHz): 9·13 (9H), 9·05 (6H), 9·03 (3H), 8·91 (3H) (all s, totally seven Me's), 7·94 (3H, s, AcO), and other signals as given in Table IV (Found: C, 79·05; H, 10·14. $C_{32}H_{50}O_3$ requires C, 79·62; H, 10·44%).

Catalytic Hydrogenation of **35a**. A solution of **35a** (80 mg) in EtOH (15 ml) was hydrogenated over Raney Ni (W-7) (100 mg) at room temp for 12 hr. The product obtained after the usual work up was separated by prep. TLC developing with n-hexane-AcOEt (4:1) to afford **40** (40 mg) and erythrodiol (**8a**, 28 mg). Recrystallization from MeOH gave a pure sample of 3β-hydroxy-13β,28-epoxy-oleanane (**40**) of m.p. 251–252°; $[\alpha]_D$ + 47° ($CHCl_3$); ν_{max} ($CHCl_3$): 3610, 3470 cm^{-1}; NMR (60 MHz): 9·22 (3H), 9·12 (6H), 9·09 (3H), 9·01 (6H), 8·80 (3H) (all s, totally seven Me's), and other signals as given in Table V (Found: C, 81·58; H, 11·44. $C_{30}H_{50}O_2$ requires C, 81·39; H, 11·38%).

Oxidation of 3,16,22,28-*tetra*-O-*acetyl-dihydropriverogenin A* (**10b**). To a stirred solution of **10b** (745 mg) in dry CCl_4 (25 ml), was added dropwise a mixture of t-butyl chromate-CCl_4 solution (25 ml),[26] AcOH (9 ml), and Ac_2O (4 ml) and the mixture was refluxed for 2 hr and treated with aq. oxalic acid solution and then with crystals of oxalic acid to decompose excess t-butyl chromate. The mixture was extracted with CCl_4 and the organic layer washed with water, aq. 5% $NaHCO_3$, and water successively and treated in the usual way. The dark brown crude product was purified by silica gel (35 g) column chromatography eluting with C_6H_6-$CHCl_3$ (1:1) to afford **41** (710 mg). Recrystallization from aq. EtOH gave pure 3,16,22,28-tetra-O-acetyl-11-keto-dihydropriverogenin A (**41**) m.p. 225–227° (colorless needles); $[\alpha]_D$ −2° ($CHCl_3$); ν_{max} ($CHCl_3$): 1735, 1248 (acetate), 1657 (enone) cm^{-1} (Found: C, 69·23; H, 8·44. $C_{38}H_{56}O_9$ requires C, 69·48; H, 8·59%).

LAH reduction of **41** *followed by treatment with hot* MeOH. To a solution of LAH (500 mg) in dry ether (20 ml), was added dropwise a solution of **41** (300 mg) in dry ether (20 ml) and the total was refluxed for 3 hr. After cooling the mixture was treated with MeOH and aq. 10% NaOH in the usual manner and extracted with ether. Work up gave unstable 11ξ-hydroxy-dihydropriverogenin A (**42**, 170 mg). Without purification, **42** was treated with hot MeOH to give crystals, shown to be a mixture of **43a** and a small quantity of the diene (**44**) (UV). Further recrystallization from MeOH afforded a pure sample of **43a** (83 mg, colorless needles) m.p. 255–257°; $[\alpha]_D$ + 20° ($CHCl_3$); ν_{max} (KBr): 3440 cm^{-1} (Found: C, 74·70; H, 10·31. $C_{30}H_{48}O_4 \cdot \frac{1}{2}H_2O$ requires C, 74·73; H, 10·17%).

Acetylation of **43a**. Treatment of **43a** (42 mg) with Ac_2O (2 ml) and pyridine (3 ml) furnished the acetate (**43b**) colorless needles from MeOH, m.p. 259–260°; $[\alpha]_D$ + 29° ($CHCl_3$); ν_{max} ($CHCl_3$): 3600, 3490, 1722, 1243 cm^{-1}; NMR (60 MHz): 9·14 (6H), 9·07 (3H), 8·99 (6H), 8·90 (3H), 8·70 (3H) (all s, totally seven Me's), 7·95 (6H, s, two AcO's), and the other signals as given in Table V. (Found C, 72·80; H, 9·33. $C_{34}H_{52}O_6$ requires C, 73·38; H, 9·41%).

Catalytic hydrogenation of **43a**. A solution of **43a** (26 mg) in EtOH (8 ml) was hydrogenated over Raney Ni (W-7) (70 mg) at room temp for 4 hr. After work up, the product was recrystallized from acetone-CCl_4 to give crystals (19 mg), identified with priverogenin B (**9**) by m.m.p., IR, and TLC.

Acknowledgements—The authors would like to express their sincere thanks to the Res. Lab. of Takeda Chemical Industries for measuring the NMR spectra (100 MHz), to the Res. Lab. of Dainippon Pharmaceutical Co. for the elemental analyses, and to Prof. R. Tschesche of Bonn University, Germany for his generous gift of priverogenin B.

REFERENCES

[1] E. E. van Tamelen, *Fortschritte der Chemie Organischer Naturstoffe*, Vol. 19, p. 243 ed. by L. Zechmeister, Springer-Verlag, Vienna, (1961)

[2] T. Kato and Y. Kitahara, *J. Synth. Org. Chem. Japan* **28**, 559 (1970)

[3] [a] K. Schaffner, *Fortschritte der Chemie Organischer Naturstoffe*, Vol. 22, p. 1, ed. by L. Zechmeister, Springer-Verlag, Vienna (1964); [b] *Organic Photochemistry*, Vol. 1 and 2, ed. by O. L. Chapmann, Marcel Dekker, Inc., New York (1967 and 1969)

[4] P. G. Sammes, *Quart. Rev.* **24**, 37 (1970)

[5] I. Kitagawa, K. Kitazawa, K. Aoyama, M. Asanuma and I. Yosioka, *Tetrahedron* (following paper)

[6] [a] T. Murata, S. Imai, M. Imanishi, M. Goto and K. Morita, *Tetrahedron Letters* 3215 (1965); [b] T. Murata, S. Imai, M. Imanishi and M. Goto, *Yakugaku Zasshi* **90**, 744 (1970)

[7] M. Nishikawa, K. Kamiya, T. Murata, Y. Tomiie and I. Nitta, *Tetrahedron Letters* 3223 (1965)

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

[9] [a] R. Tschesche, B. T. Tjoa and G. Wulff, *Liebigs Ann.* **696**, 160 (1966); [b] Idem, *Tetrahedron Letters* 183 (1968); [c] I. Yosioka, T. Nishimura, A. Matsuda and I. Kitagawa, *Chem. Pharm. Bull. (Tokyo)* **19**, 1186 (1971)

[10] [a] H. Itokawa, N. Sawada and T. Murakami, *Ibid* **17**, 474 (1969); [b] S. Ito, M. Kodama and M. Konoike, *Tetrahedron Letters* 591 (1967); [c] I. Yosioka, A. Matsuda, T. Nishimura, S. Hirai and I. Kitagawa, *Chem. Pharm. Bull. (Tokyo)* **15**, 1435 (1967); [d] M. Kodama and S. Ito, *Chem & Ind.* 1647 (1967)

[11] I. Kitagawa, K. Kitazawa and I. Yosioka, *Tetrahedron Letters* 509 (1968)

[12] D. H. R. Barton and N. J. Holness, *J. Chem. Soc.* 78 (1952)

[13] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Structure Elucidation of Natural Products by Mass Spectrometry*, Vo. 2, p. 122 Holden-Day, Inc., San Francisco, (1964)

[14] K. Nakanishi, *Infrared Absorption Spectroscopy*, p. 36, Holden-Day, Inc., San Francisco and Nankodo Co. Ltd., Tokyo, (1962)

[15] [a] N. S. Bhacca and D. H. Williams, *Applications of NMR Spectroscopy in Organic Chemistry*, p. 99, Holden-Day, Inc., San Francisco, (1964); [b] Idem, *Ibid.* p. 82; [c] K. Tori, K. Komeno and T. Nakagawa, *J. Org. Chem.* **29**, 1136 (1964)

[16] [a] F. H. Newth, *Quart. Rev.* **13**, 30 (1959); [b] E. L. Eliel, N. S. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis*, p. 343, John Wiley and Sons, Inc., New York, (1965)

[17] D. H. R. Barton, E. F. Lier and J. F. McGhie, *J. Chem. Soc. (C)* 1031 (1968)

[18] J. F. Fried, J. W. Brown and M. Applebaum, *Tetrahedron Letters* 849 (1965)

[19] I. Kitagawa, K. Kitazawa and I. Yosioka, *Ibid.* 2643 (1968)

[20] [a] R. O. Dorchai and J. B. Thomson, *Tetrahedron Letters* 2223 (1965); [b] N. Aimi, H. Fujimoto and S. Shibata, *Chem. Pharm. Bull. (Tokyo)* **16**, 641 (1968); [c] T. Kubota and H. Hinoh, *Tetrahedron* **24**, 675 (1968); [d] R. Tschesche, B. Tjiong and G. Wulff, *Liebigs Ann.* **696**, 160 (1966); [e] R. C. Cookson, T. A. Crabb, J. J. Frankel and J. Hudec, *Tetrahedron Supplement* No. 7, 355 (1966)

[21] R. Tschesche, F. Inchaurrondo and G. Wulff, *Liebigs Ann.* **680**, 107 (1964)

[22] I. Kitagawa, K. Kitazawa and I. Yosioka, *Chem. Pharm. Bull (Tokyo)* **16**, 2304 (1968)

[23] R. Tschesche, H. Striegler and H. W. Fehlhaber, *Leibigs Ann.* **691**, 165 (1966)

[24] I. Kitagawa, A. Matsuda and I. Yosioka, *Tetrahedron Letters* 5377 (1968)

[25] H. T. Cheung and L. Tökes, *Ibid.* 4363 (1968)

[26] K. Heusler and A. Wettstein, *Helv. Chim. Acta* **35**, 284 (1952)