ACID-CATALYZED REARRANGEMENTS OF AN A(1)-NOR-TRITERPENOID 2α,3α-EPOXIDE*

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Reactions of 2α,3α-epoxide *X*, derived from 19β,28-epoxy-A(1)-nor-18α-oleanane, with acids proceed with migration of the 10β-methyl group into the position 2β, giving rise to unsaturated alcohols *XII* and *XIV* and diene *IX*. Reaction with boron trifluoride etherate afforded ketone *XI* in addition to *XII* and *XIV*. Olefin *VIII* rearranged in acidic medium to give olefins *XXVI* and *XXVII*. The rearranged products were converted into other derivatives and their structure was established by ^{1}H and ^{13}C NMR, IR, UV and mass spectra.

As a part of our stereochemical studies of the ring A in triterpenoids, we described previously[1] some derivatives of 19β,28-epoxy-A(1)-nor-18α-oleanane with substituents in positions 2 and 3 of the five-membered ring A. Extending this work, we tried now to prepare further 2,3-disubstituted A(1)-nor-derivatives (such as *trans*-bromohydrins, diols etc.) by acid-catalyzed opening of 2α,3α-epoxide *X* or by addition reactions to the 2(3)-double bond in olefin *VIII*. Similar methods have been successfully applied to analogous compounds containing six-membered ring A (see e.g. refs[2,3]). In the present communication we show that these reactions of derivatives with the five-membered A-ring are accompanied by a shift of the 10β-methyl group from C-10 to C-2.

The olefin *VIII* and epoxide *X* were prepared from 19β,28-epoxy-18α-oleanan-3-one (*I*) via dibromoketone *II*, hydroxy acid *III*, ketone *IV* and alcohols *V* and *VI*, using the known[1] procedure. Large-scale preparation of olefin *VIII* without purification of the intermediates allowed the isolation of some side-products (*VII*, *XXVIII*) that were utilized for spectral studies of A-nor-derivatives. Reaction of a mixture of isomeric alcohols *V* and *VI* (obtained by sodium borohydride reduction of ketone *IV*) with phosphorus oxychloride in pyridine[1] afforded small amount of the 3α-chloro derivative *VII* (2%) in addition to *VIII*. Configuration of the chlorine atom follows

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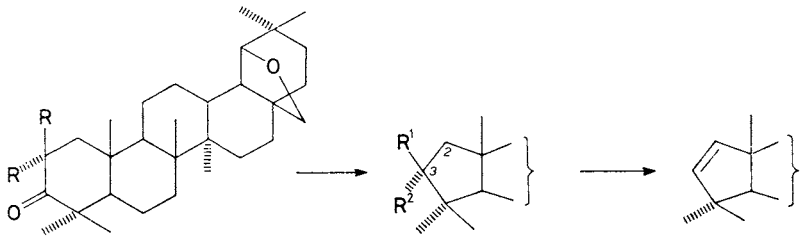
from the ^{1}H NMR spectrum in which the coupling constants $J(2, 3) = 10{\cdot}3$ and 7·0 Hz correspond to $J(2\alpha, 3\beta)$ and $J(2\beta, 3\beta)$, respectively[1]. When the olefin *VIII* was prepared from the crude ketone *I* (contaminated with the corresponding E-ring lactone (3-oxo-18α-oleanan-28→19β-olide)), minor quantities of lactone *XXVIII* with the 2(3)-double bond were obtained. Its structure was confirmed by IR (1 762 cm^{-1}, γ-lactone) and ^{1}H NMR spectra (3·93 s, H-19; 5·47 d and 5·97 d, J = 5·7 Hz, H-2 and H-3).



I, R = H
II, R = Br

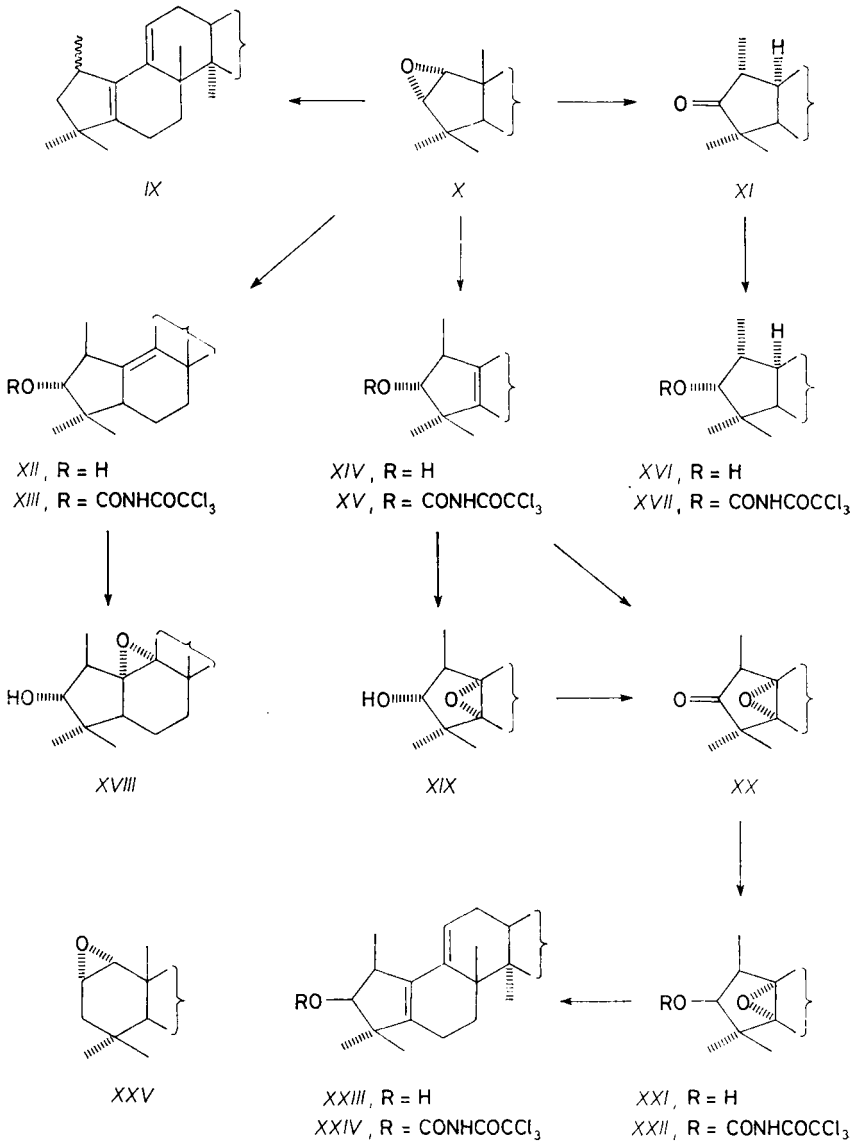
III, R^1 = OH; R^2 = COOH
IV, R^1 + R^2 = O
V, R^1 = OH; R^2 = H
VI, R^1 = H; R^2 = OH
VII, R^1 = H; R^2 = Cl

VIII

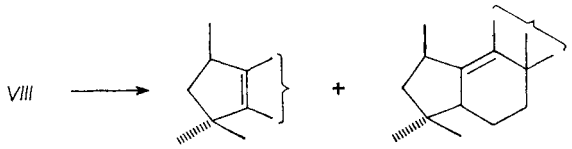
Reaction of epoxide *X* with hydrobromic acid led to a mixture from which we isolated diene *IX* and unsaturated alcohol *XIV*. Thin-layer chromatography showed also minor amounts of the isomeric alcohol *XII*. On treatment with perchloric acid in aqueous dioxane, epoxide *X* was converted into a mixture of alcohols *XII* and *XIV* with the latter highly predominating. The same mixture of alcohols was obtained by reaction of *X* with acetic acid at room temperature as well as at reflux. As side-products we detected (TLC) less polar compounds, most probably acetates of *XII* and *XIV*, because on alkaline hydrolysis they afforded mixture of these alcohols. Alcohols *XII* and *XIV* were also formed on treatment with acetic acid containing 5% of sodium acetate. Reaction of *X* with boron trifluoride etherate in benzene at room temperature gave alcohols *XII* and *XIV* together with ketone *XI*. When the reaction was performed in boiling benzene, the ketone *XI* was accompanied by an unseparable mixture of dienes which were not identified.

To determine the structure of products and to compare the spectral data, we reduced the ketone *XI* with sodium borohydride to alcohol *XVI*. Alcohols *XII* and *XIV* were converted into epoxy alcohols *XVIII* and *XIX* with 3-chloroperoxybenzoic acid. Oxidation of alcohol *XIV* with sodium dichromate in acetic acid in the presence of sodium acetate led to epoxy ketone *XX* which was also prepared by oxidation of epoxy alcohol *XIX* with the same reagent. Epoxy ketone *XX* was

reduced with sodium borohydride to afford epoxy alcohol *XXI* as the principal product, along with negligible amount of the 3α-isomer *XIX*. Compound *XXI* with *trans*-relation of the hydroxy and the epoxide groups is very unstable compared with the *cis*-isomer *XIX* and the epoxy ketone *XX*: in the presence of traces of acids (e.g. in the work-up of the reaction mixture after reduction of ketone *XX*, during crystallization, chromatography, etc.) the epoxide group reacts under elimina-



tion of water, the 3β-hydroxyl being intact, and the product is dienol *XXIII*. For comparison with the reactions of epoxide *X* we also investigated the acid-catalyzed isomerization of olefin *VIII*. In boiling formic acid it rearranged to give the isomeric



XXVI *XXVII*

TABLE I

Proton NMR parameters (δ in ppm, J in Hz) of 25(10→2) *abeo*-A(1)-nor-triterpenoid derivatives

δ(H) J(H, H)	*IX*[a]	*XI*	*XII*[b]	*XIII*	*XIV*[c]	*XV*	*XVI*[d,e]	*XVII*[f]
$\delta(CH_3)$	0·834	0·814	0·774	0·799	0·814	0·819	0·808	0·810
	0·845	0·937	0·807	0·867	0·852	0·857	0·878	0·887
	0·934	0·937	0·845	0·872	0·896	0·916	0·914	0·935
	0·955	0·964	0·944	0·943	0·941	0·940	0·928	0·973
	1·019	0·996	1·014	1·029	0·959	1·004	0·936	1·004
	1·053	1·009	1·102	1·112	1·016	1·125	0·978	1·075
$\delta(CH_3$-25)	1·010	1·168	1·182	1·274	1·126	1·194	0·955	0·916
J(25, 2)	6·9	6·9	7·6	7·6	7·2	7·2	7·4	7·6
δ(H-2)	2·87	2·44	2·61	2·76	2·43	2·60	2·35	2·63
J(2, 3)	9·0; 2·5	—	≈0	≈0	1·8	0·8	9·6	9·6
J(2, 10)	—	11·0	—	—	—	—	7·6	7·5
δ(H-3)	1·96; 1·40	—	3·44	4·61	3·44	4·71	3·96	5·04
δ(H-6α, 6β)	1·98	*m*	*m*	*m*	1·87	1·91	*m*	*m*
δ(H-9)	—	*m*	—	—	2·52	2·52	1·94	1·97
J(9, 11β)	—	*m*	—	—	13·5	13·5	*m*	*m*
J(9, 11α)	—	*m*	—	—	2·7	2·7	*m*	*m*
δ(H-19)	3·54	3·54	3·54	3·55	3·57	3·58	3·55	3·55
δ(H-28*endo*)	3·85	3·78	3·83	3·84	3·81	3·81	3·79	3·80
δ(H-28*exo*)	3·49	3·45	3·47	3·48	3·46	3·47	3·45	3·46
J(28, 28)	7·8	7·8	7·8	7·8	7·8	7·8	7·9	7·8
δ(NH)	—	—	—	8·33	—	8·39	—	8·37

[a] J(3, 3) = 13·0 Hz; J(6α, 2) = J(6β, 2) = 1·8; H-11: 5·37 dd, J(11, 12β) = 5·2; J(11, 12α) = = 2·5, H-12β: 2·30 dt, J(12, 12) = 17·7; J(12β, 11) = J(12β, 13) = 5·2. [b] J(2, 11α) = J(2, 11β)= = 1·5, [c] J(2, 6α) = J(2, 6β) = J(2, 9) = 1·8. [d] H-10: 2·02 dt, J = 7·6; ~6; ~6. [e] In hexadeuterobenzene–pentadeuteropyridine (2 : 1), H-2: 2·40 m, J(2, 3) = 9·8; J(2, 10) = 8·1; J(2, 25) = 7·0, H-9: 1·83 ddd, J(9, 10) = 6·0; J(9, 11β) = 12·1; J(9, 11α) = 4·2, H-10: 2·03 m, J(10, 2) = 8·1; J(10, 9) = 6·0; J(10, 5) = 7·1. [f] H-10: 2·16 m, J = 7·5; 6·6; 6·6.

olefins *XXVI* and *XXVII* in an approximately 1 : 1 ratio (according to NMR spectra).

Structure of the obtained 25(10→2)*abeo*-A(1)-nortriterpenoids follows from the ^{1}H NMR (Table I), ^{13}C NMR (Table II), infrared (Table III), ultraviolet and mass spectra. To facilitate signal assignment in the NMR spectra of alcohols *XII*, *XIV*, *XVI*, *XXI* and *XXIII*, we measured also spectra of their respective trichloroacetylcarbamoyl (TAC) derivatives *XIII*, *XV*, *XVII*, *XXII* and *XXIV*, prepared by in situ reaction[4,5] with trichloroacetyl isocyanate (TAI). The TAI acylation-induced shifts, $\Delta\delta$(TAC), of the A-ring protons are given in Table IV.

TABLE I (*Continued*)
in deuterochloroform

XIX[g]	*XX*	*XXI*	*XXII*	*XXIII*[h]	*XXIV*[i]	*XXVI*[j]	*XXVII*[k]
0·811	0·814	0·808	0·808	0·827	0·831	0·805	0·611
0·858	0·873	0·847	0·858	0·844	0·848	0·812	0·810
0·870	0·945	0·883	0·907	0·932	0·950	0·913	0·819
0·940	0·972	0·927	0·936	0·953	0·950	0·940	0·944
1·035	1·077	0·939	1·097	0·971	1·102	0·940	0·981
1·064	1·123	1·033	1·097	1·066	1·127	1·022	1·096
1·140	1·249	0·996	0·965	0·971	0·954	1·005	1·044
7·6	7·8	7·6	7·4	7·2	7·1	6·7	6·8
2·34	2·63	2·48	2·90	2·96	3·28	2·54	2·56
≈0	—	7·1	7·4	8·2	8·2	8·7; [m]	8·2; [m]
—	—	—	—	—	—	—	—
3·15	—	3·65	4·62	4·00	5·04	1·90; [m]	1·70; [m]
[m]	[m]	[m]	[m]	2·00	2·02	1·85	[m]
2·28	2·38	2·28	2·31	—	—	2·39	—
13·9	14·0	14·0	13·8	—	—	12·8	—
3·4	3·4	3·2	3·2	—	—	2·9	—
3·55	3·56	3·56	3·56	3·54	3·54	3·59	3·56
3·77	3·79	3·77	3·77	3·85	3·85	3·81	3·84
3·46	3·47	3·45	3·46	3·49	3·50	3·46	3·47
7·9	7·9	7·9	7·9	7·8	7·8	7·9	7·8
—	—	—	8·33	—	8·39	—	—

[g] OH: 2·44 d, J(OH, 3) = 12·2. [h] J(2, 6α) = J(2, 6β) = 1·8, H-11: 5·40 dd, J(11, 12β) = 5·0; J(11, 12α) = 2·5, H-12β: 2·31 dt, J(12, 12) = 18·0; J(12β, 11) = J(12β, 13) = 5·0. [i] H-11: 5·42 dd, J(11, 12β) = 5·0; J(11, 12α) = 2·5, H-12β: 2·32 bdt, J(12, 12) = 18·0; J(12β, 11) = = J(12β, 13) = 5·0. [j] J(3, 3) = 12·3. [k] J(3, 3) = 12·4, H-5: 2·36 m, J(5, 6α) = 4·6; J(5, 6β) = = 13·9; J(5, 11) = 2·3. [m] The value of the parameter could not be determined.

Proton NMR spectra of all the 25(10→2)*abeo* compounds exhibit only six singlets of skeletal methyl groups; the seventh (CH_3-25) occurs as a doublet (J = 6·7 to 7·8 Hz). From the mechanistic viewpoint, opening of the 2α,3α-epoxide group in *X* and shift of the 10β-methyl group to C-2 should lead to *trans*-relation of the methyl (2β) and hydroxyl (3α) groups. This configuration is compatible with the low J(2, 3)

TABLE II

Carbon-13 NMR chemical shifts (in ppm) of 25(10→2)*abeo*-A(1)-nor-triterpenoid derivatives

Carbon	*IX*	*XI*	*XII*	*XIII*	*XIV*	*XV*	*XVI*
C-2	36·13	38·87	45·00	42·74	49·09	46·95	38·59
C-3	47·74	213·75	89·08	94·65	88·04	92·80	79·52
C-4	45·40	49·41	43·61	43·62	47·59	47·62	44·14
C-5	136·59	45·95	49·37	50·10	137·64*	137·77*	48·98
C-6	18·89	28·57	20·22	20·06	19·07	18·83	22·23
C-7	28·55	30·89	31·72	31·43	28·77	28·66	30·86
C-8	37·26	39·77*	43·61	43·62	39·10**	39·13**	39·96
C-9	142·15	47·50**	140·05	138·46	40·59	40·36	47·49
C-10	137·30	44·02	135·03	135·81	137·22*	137·49*	36·15
C-11	118·55	22·13	27·28	27·79	26·20***	26·30***	27·93
C-12	28·08	26·65	26·84	27·29	27·32	27·35	26·53
C-13	31·19	34·73	34·05	34·00	34·61	34·68	34·79
C-14	39·80	40·38*	39·80	39·85	39·19**	39·21**	39·25
C-15	26·65	26·33	26·33	26·23	26·07***	26·02***	26·44
C-16	36·76	36·73	36·72	36·71	36·70	36·70	36·75
C-17	36·23	36·27	36·31	36·29	36·27	36·27	36·28
C-18	47·92	46·77**	47·28	47·30	46·45	46·46	46·82
C-19	88·21	87·88	88·17	88·16	87·86	87·86	87·94
C-20	41·71	41·51	41·63	41·59	41·51	41·52	41·52
C-21	32·70	32·68	32·73	32·71	32·68	32·70	32·72
C-22	25·99	26·13	26·11	26·07	26·14	26·12	26·16
C-23[c]	28·59	25·69	22·63	22·31	26·49	26·76	23·12
C-24[c]	28·40	19·06	22·01	22·03	20·27	20·87	22·71
C-25[c]	21·19	18·96	22·01	22·00	20·22	20·04	18·33
C-26[c]	19·74	15·36	20·42	19·98	13·04	13·11	14·13
C-27[c]	14·34	13·17	15·86	15·95	13·10	13·11	12·99
C-28	70·99	71·24	71·09	71·01	71·33	71·26	71·30
C-29	24·57	24·58	24·56	24·51	24·58	24·57	24·59
C-30	28·78	28·80	28·81	28·79	28·81	28·80	28·82

[a] Data obtained in $CDCl_3$–CD_3OD (5 : 1). [b] The overlapping signals with + and − amplitude at δ 39·77 and 47·91 were resolved in the mixture of $CDCl_3$ and CD_3OD (see *XXIII*[a]).

value (0–1·8 Hz) for compounds *XII–XV* and *XIX*, low downfield TAI-acylation shifts of the H-2 signals and downfield $\Delta\delta$ (TAC) shift of the methyl in position 2 in *XII* and *XIV* (Table IV). On the other hand, spectra of 3β-compounds (*XXI* to *XXIV*) exhibit $J(2, 3) = 7{\cdot}1-8{\cdot}2$ Hz typical for *cis*-arrangement[1], higher $\Delta\delta$(TAC) H-2 values and an upfield shift $\Delta\delta$(TAC) of the methyl group.

TABLE II (*Continued*)

in deuterochloroform. Signals with the same number of asterisks can be interchanged

XIX	*XX*	*XXI*	*XXIII*	*XXIII*[a]	*XXVI*	*XXVII*
46·28	42·70	38·96	39·77[b]	39·81	37·52	33·13
87·75	220·70	78·07	80·97	80·74	44·79	40·29*
44·20	48·90	42·17	47·91[b]	47·85	48·10	50·10
75·14*	71·51*	72·51*	134·77	134·70	139·24	50·70
17·48	17·34	17·91	18·94	18·85	19·09	19·39
27·34	27·25	27·29	28·50	28·46	28·85	31·01
37·78	37·77	37·58	37·26	37·25	36·76	42·65
43·24	48·35	43·46	139·85	139·97	37·63	141·66
74·04*	68·74*	71·48*	136·89	136·93	138·76	132·80
25·06	24·82	24·89	119·03	118·79	23·65	24·96
25·83	26·09	26·46	27·56	27·52	27·32	27·43
35·08	35·04	35·12	31·14	31·14	34·79	34·84
39·24	39·33	39·30	39·77[b]	39·75	39·21	40·20*
26·33	26·23	26·22	25·96	25·83	26·27	26·70
36·60	36·64	36·61	36·73	36·60	36·76	36·77
36·29	36·31	36·28	36·23	36·16	36·29	36·32
46·57	46·31	46·30	47·91[b]	47·88	46·51	47·29
87·84	87·87	87·95	88·16	88·44	87·79	88·12
41·48	41·54	41·51	41·72	41·69	41·60	41·71
32·63	32·67	32·65	32·68	32·60	32·73	32·75
26·10	26·17	26·11	26·53	26·45	26·15	26·20
24·10	22·08	22·05	26·38	26·25	28·88	27·19
18·30	18·06	18·58	21·45	21·46	28·32	22·42
17·57	15·64	14·68	19·76	19·67	22·11	21·93
14·64	14·78	13·31	14·29	14·19	13·03	20·84
13·26	13·30	10·05	12·69	12·74	12·69	14·94
71·26	71·28	71·28	70·98	70·96	71·46	71·14
24·58	24·58	24·59	24·56	24·46	24·59	24·58
28·77	28·78	28·79	28·78	28·63	28·84	28·82

[c] Carbon signals C-23 to C-27 of the five methyl groups could not be assigned unambiguously and are presented with descending δ-values.

The assignment of structures *XII* and *XIV* to the isomeric unsaturated alcohols is based on chemical shifts of olefinic carbon atoms: for *XII* with the 9(10)-double bond the shifts of both the carbon signals significantly differ (δ 140·05 and 135·03) whereas in *XIV*, in which the 5(10)-double bond is placed symmetrically relative to the rings A and B, the shifts of these carbon signals are practically identical (δ 137·64 and 137·22). Similar situation was also observed with the corresponding TAC--derivatives *XIII* and *XV*. A convincing proof of the position of the double bond in isomers *XII* and *XIV* has come from the infrared spectra in the OH-stretching region (Table III). Spectrum of alcohol *XII* displays only a free hydroxyl band whereas that of the isomer *XIV* shows an additional weak band corresponding to

TABLE III

Frequencies and intensities of OH stretching vibrations in IR spectra. Spectra were measured on a Unicam SP-700 spectrometer in tetrachloromethane (c 2 . 10^{-3} mol l^{-1}); f free, b bonded; $B = (\pi/2)\,\Delta\nu_{1/2}\varepsilon$

Compound	$\tilde{\nu}$(OH) cm^{-1}	$\Delta\tilde{\nu}_{1,2}$ cm^{-1}	ε $l\,mol^{-1}\,cm^{-1}$	B . 10^{-3} $l\,mol^{-1}\,cm^{-2}$
XII	f 3 624	17	80	2·1
XIV[a]	f 3 623	23	41	1·5
	b 3 597	31	14	0·7
XVIII	f 3 624	18	59	1·7
XIX	b 3 542	40	68	4·3

[a] After separation.

TABLE IV

TAI-Acylation shifts of some protons on the A ring

Alcohol	Relative configuration of OH and CH_3-25 groups	$\Delta\delta$(TAC)[a]		
		CH_3-25	H-2	H-3
XII	*trans*	0·09	0·15	1·17
XIV	*trans*	0·07	0·17	1·27
XVI	*cis*	−0·04	0·28	1·07
XXI	*cis*	−0·03	0·42	0·97
XXIII	*cis*	−0·02	0·32	1·04

[a] $\Delta\delta$(TAC) = δ(TAC-derivative) − δ(alcohol).

hydrogen bond[6] to π-electrons of the 5(10)-double bond. More pronounced differences were observed for the epoxy alcohols *XVIII* and *XIX*: the 9(10)-epoxide *XVIII* has only a free hydroxyl band whereas the epoxide *XIX* has no free hydroxyl band but only a strong band of hydroxyl bonded to the suitably situated *n*-electrons of the epoxide oxygen atom (for an analogy see ref.[6]). In accord with this strong hydrogen bond the signals of OH (δ 2·44) and H-3 (δ 3·15) in the ^{1}H NMR spectrum of *XIX* occur as doublets and their vicinal coupling constant (J(3, OH) = 12·2 Hz) corresponds to an antiperiplanar arrangement of these protons on the C(3)—O bond, necessary for hydrogen bond formation to the epoxide oxygen atom. Temperature change from 22°C to 50°C resulted in an only negligible upfield shift of the OH signal (0·03 ppm) without any change in the spectral shape or the J(3, OH) value. The zero value of J(2, 3) is in accord with a slight deformation of the five-membered ring A due to the hydrogen bond (according to molecular models, the torsion angle between H-2α and H-3β is close to 90°).

The presence of intramolecular hydrogen bond in the epoxy alcohol *XIX* confirms the α-configuration of the 5,10-epoxy group in compounds *XIX*–*XXII*. For the 9(10)-epoxide *XVIII* the α-configuration can be derived using the rule of α-attack and by analogy with compound *XIX*. The position of the double bond in the isomeric olefins *XXVI* and *XXVII* follows from the similarity of their ^{1}H NMR and ^{13}C NMR spectra with those of the unsaturated alcohols *XIV* and *XII*, particularly from chemical shifts of the sp^2-carbon atoms, from the same effects of the double bonds on chemical shifts of protons next to the ether bridge in the ring E (H-19, H-28) etc. Assuming that after rearrangement of the 10β-methyl group there is no subsequent acid-catalysed isomerization in position 2, we can assign the 2β-methyl structures *XXVI* and *XXVII* to the olefins.

The ^{13}C NMR spectra of dienes *IX* and *XXIII* show the presence of one tetrasubstituted and one trisubstituted double bond (three signals of sp^2-carbon atoms in the region δ 135–142 with positive amplitude in the attached proton test[7] (APT) spectrum and one signal at δ 119 with negative APT-amplitude). The ^{1}H NMR spectra display an olefinic proton signal at δ ~ 5·40 (H-11) as a doublet of doublets and further a doublet of triplets due to one of the allylic protons (δ ~ 2·30; H-12β). This splitting, together with the observed coupling constants (J(11, 12β) ~ 5, J(11, 12α) ~ 2·5, J(12, 12) ~ 18 and J(12β, 13) ~ 5 Hz), confirms the 9(11)-position of the double bond. Multiplet of the two further allylic protons (δ ~ 2·0,H-6) and homoallylic coupling between the H-2 and both H-6 protons (1·8 Hz) agree with the 5(10)-double bond and were also found in the spectrum of the 5(10)-unsaturated alcohol *XIV*. The UV absorption of dienes *IX* and *XXIII* (230, 238, 246 and 255 nm) corresponds to heteroannular transoid dienes of this substitution type. The configuration of the methyl group on C-2 in diene *IX* remains undetermined; in the conversion of epoxide *X* to diene *IX* a configuration change after migration of the 10β-methyl group cannot be excluded and because of flexibility of the five-

-membered ring A the configuration cannot be determined even from the observed coupling constants $J(2, 3)$ (9·0 and 2·5 Hz).

As concerns the structure and spatial arrangement of the further rearrangement product, i.e. ketone *XI*, most information was obtained from the ^{1}H NMR spectra of alcohol *XVI* (prepared from *XI*) measured in a mixture of hexadeuterobenzene and pentadeuteropyridine (2 : 1). In this solvent system it was possible to identify safely the signals of H-2, H-3, H-9, H-10 and H-25 by the selective spin-decoupling and to obtain the coupling constants important for configurational assignment. The found values of J are given in Fig. 1. The doublet of doublets of doublets at δ 1·83 (see note *e* in Table I) is ascribed to the H-9α rather than H-5α proton because this signal (δ 1·94 in deuterochloroform) exhibits a negligible TAI-acylation shift (+0·03). For the H-5α proton we should expect a higher value, comparable with that found for H-10 (+0·14). The values of $J(9, 10)$ and $J(5, 10)$ clearly show the α-configuration of H-10 and confirm the *cis*-fusion of the rings A and B.The value of $J(2, 10)$ (~8 Hz) in alcohol *XVI* and its TAC-derivative *XVII* cannot give an unequivocal information on the configuration in position 2, however, the value for the ketone *XI* (11·0 Hz) indicates *trans*-arrangement of the protons, i.e. the α-configuration of the methyl on C-2. This configuration is compatible with the observed stability of *XI* which does not change in an acidic medium (e.g. under conditions of preparation of enol acetate or enol ether). The alternative 2β-methyl ketone should be unstable due to strong non-bonding interactions of the 2β-methyl group with the 8β-methyl and 11-methylene groups: consequently an easy isomerization

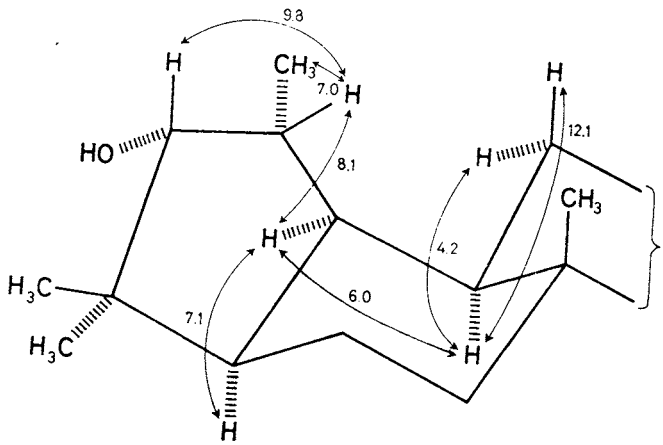


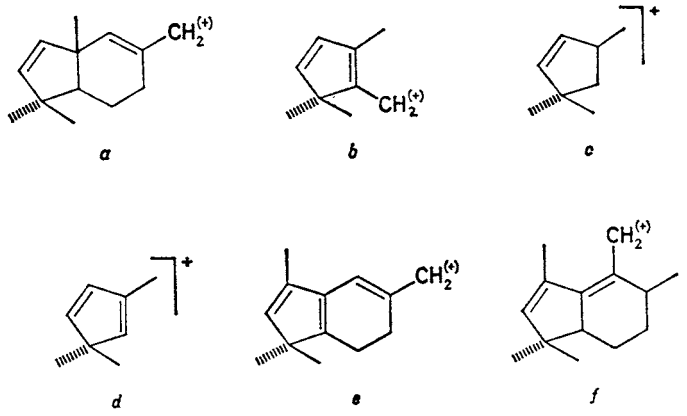
FIG. 1

Structure of alcohol *XVI* with values of J(H, H) found in hexadeuterobenzene–pentadeuteropyridine (2 : 1)

at C-2 should be observed, similarly to the case of the steroid analogue[8]. Moreover, the formation of the 2α-isomer *XI* from epoxide *X* by treatment with boron trifluoride etherate is in accord with the mechanism suggested by Yoshida[8]. This mechanism involves two 1,2-hydrogen shifts (H-2α to C-10 and H-3β to C-2) after migration of the 10β-methyl group into position 2β.

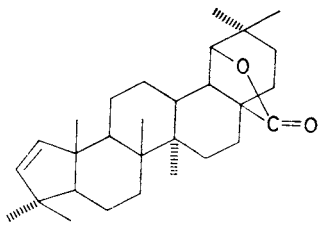
The suggested α-configuration of hydroxyl in alcohol *XVI* is based on the TAI--acylation shifts which correspond to *cis*-arrangement of OH and CH_3 groups (Table IV). Thus, in the reduction the hydride attacks the ketone *XI* from the β-side, contrary to the reduction of ketones *IV* (ref.[1]) and *XX* where the α-attack is preferred. The reason is obviously the steric crowding caused by the two α-oriented methyl groups on C-2 and C-4.

In the higher-mass region, mass spectra of the A-nor-derivatives exhibit ions arising by loss of methyl radical and water and further by loss of $C_5H_{11}^{\bullet}$ from the ring E and of $CH_2OH^{\bullet}$ from the ether bridge, that are typical[9,10] for 19β,28-epoxy--18α-oleanane compounds. Spectra of olefins *VIII* and *XXVIII* and of the chloro derivative *VII* (with unrearranged skeleton) display ions *a* (*m/z* 175) which involve rings A and B and arise by cleavage of ring C (refs[9,11]). In the spectrum of *VII* they are accompanied by ions *m/z* 211 and 213 (*a* + HCl). Other highly abundant ions, indicating the 2(3)-double bond, arise by fission of ring B and can be formulated as *b* (*m/z* 121), *c* (*m/z* 109) and *d* (*m/z* 107).

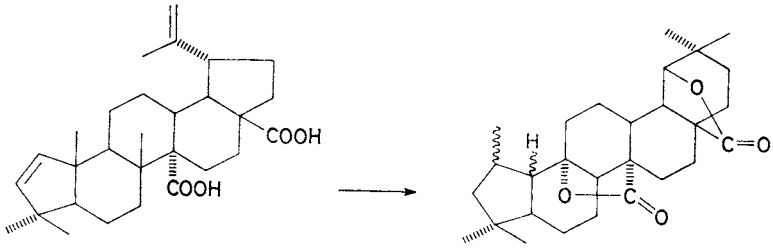


Mass spectra of the isomeric unrearranged alcohols *XII* and *XIV* are very similar. The base peak, *m/z* 173, corresponds to fragment e involving rings A and B (after loss of water molecule). Its formation from the isomer *XII* can be explained by isomerization of the 9(10)-double bond into the position 5(10) which seems to be more probable than the fission of the C(9)—C(11) vinyl bond. Another abundant ion, *m/z* 189, arises probably by cleavage of the C(11)—C(12) and C(8)—C(14)

bonds with hydrogen transfer from the neutral part and elimination of water (ion *f*). Interestingly enough, the ion *m/z* 173 occurs as the base peak also in the spectrum of epoxide *X*. Possibly, the ionization is followed by a rearrangement similar to that in the acid-catalysed conversion of the epoxide into alcohols *XII* and *XIV* and the loss of water leads then to ion e. Both the dienes *IX* and *XXIII* have very stable molecular ions, the dominant fragmentation being the loss of $CH_3^{\bullet}$. Ions arising by cleavage of ring C (*m/z* 173 and 187 for diene *IX* and *m/z* 189 and 203 for dienol *XXIII*) are relatively little abundant. The epoxy compounds *XVIII*–*XXI* do not show any specific fragmentation due to the functional groups on the rings A and B. Noteworthy is only the ion *m/z* 384 in the spectrum of *XX* that apparently arises by cleavage of bonds C(2)—C(10) and C(3)—C(4) under elimination of methylketene. A similar fragmentation was observed[9] with hydroxy acid *III* and its esters.



XXVIII



XXIX *XXX*

We may conclude that reactions of the epoxide *X* with acidic reagents are always accompanied by shift of the 10β-methyl group and the obtained mixtures do not contain any products of normal epoxide ring opening, i.e. 2,3-disubstituted derivatives. The rearrangement takes place even under very mild conditions, e.g. on treatment with acetic acid in the presence of sodium acetate at 20°C. Attempts to prepare bromohydrin formates by addition of bromine to olefin *VIII* in N,N-dimethylformamide in the presence of silver perchlorate[12] were also unsuccessful. The arising mixtures of non-polar compounds contained neither bromohydrin formates nor

other 2,3-adducts and attempted separation and purification of these compounds led to mixtures of unidentified dienes (according to mass spectra); however, the formation of dienes indicates again skeletal rearrangements.

The ease of migration of the 10β-methyl group in epoxide *X* is connected with the localization of the epoxide functionality on the five-membered ring. Analogous triterpenoid and 4,4-dimethylsteroid 1α,2α-epoxides with six-membered ring A (partial formula *XXV*) are opened by acids without rearrangement, giving rise to 1α,2β-disubstituted compounds[2,3]. A higher propensity to rearrangement of the neighbouring axial methyl group in epoxides on five-membered ring was also observed with B-norsteroid 5,6-epoxides[13–15]. On the other hand, also the cumulation of the methyl groups on the β-side of the triterpenoid skeleton (4β, 10β, 8β) in epoxide *X* plays a certain role because steroid 16α,17α-epoxides are opened with acids without migration of the neighbouring 13β-methyl group[16,17] and the reaction of 1α,2α-epoxy-A-norsteroids gives both 1,2-disubstituted compounds and products of rearrangement of the 10β-methyl group[8].

The isomerization of olefin *VIII* into compounds *XXVI* and *XXVII* has its analogy[18] in the acid-catalyzed conversion of ceanothenic acid (*XXIX*) into dilactone *XXX*. In this case one of the double bond isomers is stabilized by lactonization of the 14α-carboxyl group.

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured on an automatic polarimeter ETL-NPL (Bendix–Ericsson) in chloroform (*c* 0·3 to 0·7). Infrared spectra were recorded in chloroform on a PE 684 (Perkin–Elmer) spectrometer (wavenumbers given in cm^{-1}), UV spectra were taken in cyclohexane on a Unicam SP700 instrument. Mass spectra were obtained with a Varian MAT 311 spectrometer (ionizing electron energy 70 eV, ionizing current 1 mA, source temperature 200°C, direct inlet at 100–140°C). NMR spectra were measured at 22°C in deuterochloroform (unless stated otherwise) with tetramethylsilane as internal standard on a Varian XL-200 (FT-mode, ^1H at 200 MHz, ^{13}C at 50·31 MHz) or (when stated) on a Tesla BS 487A instrument (CW-mode, ^1H at 80 MHz). Chemical shifts and coupling constants of protons were obtained by the first order analysis from the expanded spectra (1–2 Hz/cm) using weighing functions for better resolution. Structural assignments to coupled protons were made using the homonuclear spin-decoupling. Trichloroacetylcarbamoyl derivatives were prepared in NMR tubes by addition of a slight excess of trichloroacetyl isocyanate to a solution of the alcohol[4,5]. Chemical shifts of the ^{13}C atoms were referenced to $CDCl_3$ using the relation $\delta(CDCl_3) = 77{\cdot}0$. The number of directly bonded hydrogen atoms was determined by the "proton decoupled attached proton test" spectra[7].

Column chromatography was carried out on silica gel (Silpearl, Kavalier, Votice), thin-layer chromatography (TLC) on silica gel G according to Stahl (Merck), detection by spraying with 10% sulfuric acid and heating, or on Silufol sheets (Kavalier, Votice), detection with 5% solution of phosphomolybdic acid in ethanol and heating. Preparative HPLC was carried out on an apparatus consisting of a Consta-Metric I pump (LDC), a Knauer "injection valve" and a refractometric detector RIDK-101 (Laboratorní přístroje, Prague). The separations were performed

on an 8 × 200 mm column packed with silica gel (particle size 7 μm, SI-VSK, Laboratorní přístroje, Prague), mobile phase heptane with 0·75% of ethyl acetate.

"The usual work-up procedure" denotes partition of the reaction mixture between water and ether, washing the ethereal phase with water, 5% sodium carbonate solution and water, drying over anhydrous sodium sulfate and evaporation of the solvents. The identity of the compounds was confirmed by melting point, mixture melting point, IR spectra and TLC. Analytical samples were dried over phosphorus pentoxide at 100°C under reduced pressure.

3α-Chloro-19β,28-epoxy-A(1)-nor-18α-oleanane (*VII*) and
19β,28-Epoxy-A(1)-nor-18α-olean-2-ene (*VIII*)

A mixture of alcohols *V* and *VI*, obtained by reduction of ketone *IV* with sodium borohydride, was treated with phosphorus oxychloride in boiling pyridine according to ref.[1]. Chromatography on silica gel in light petroleum afforded olefin *VIII* (75%), m.p. 214–217°C (reported[1] m.p. 216–218°C). Mass spectrum, *m/z* (%): 410 (M^+, 6), 395 (30), 379 (41), 339 (3), 327 (9), 203 (10), 189 (15), 175 (58), 173 (29), 121 (87), 109 (78), 107 (100). Further elution gave chloro derivative *VII* (2%); m.p. 192–196°C (chloroform–methanol), $[\alpha]_D$ +40°. IR spectrum: 1 032 (C—O). ^{1}H NMR spectrum (80 MHz): 0·80 s, 3 H; 0·84 s, 3 H; 0·94–0·96 bs, 9 H; 1·04 s, 3 H and 1·06 s, 3 H (7 × CH_3); 2·25 dd, 1 H (H-2β, $J(2, 2') = 11·5$, $J(2\beta, 3\beta) = 7·0$); 3·43 d, 1 H and 3·78 bd, 1 H (H_2-28, $J(28, 28') = 8$); 3·52 s, 1 H (H-19); 4·19 dd, 1 H (H-3β, $J(2\alpha, 3\beta) = 10·3$; $J(2\beta, 3\beta) = 7·0$). Mass spectrum, *m/z* (%): 448 (M^+ +2, 12), 446 (M^+, 32), 417 (12), 415 (18), 410 (43), 395 (39), 377 (23), 375 (41), 213 (35), 211 (88), 205 (55), 203 (44), 191 (58), 189 (56), 177 (82), 175 (95), 149 (65), 121 (100), 109 (76), 107 (91). For $C_{29}H_{47}ClO$ (447·2) calculated: 77·90% C, 10·59% H; found: 77·74% C, 10·37% H.

2α,3α; 19β,28-Diepoxy-A(1)-nor-18α-oleanane (*X*)

The compound was prepared according to ref.[1]. Mass spectrum, *m/z* (%): 426 (M^+, 6), 411 (8), 408 (10), 395 (13), 393 (11), 355 (15), 255 (7), 189 (25), 173 (100).

Reactions of Epoxide *X*

a) *With hydrobromic acid.* A solution of epoxide *X* (115 mg) in chloroform (3 ml) was shaken with 48% hydrobromic acid (8 ml) for 2 h and then processed in the usual manner. The residue consisted (TLC) of diene *IX*, alcohol *XIV*, minor amounts of alcohol *XII*, and further unidentified compounds. Preparative TLC on silica gel in light petroleum–ether (6 : 1) afforded *XIV* (25 mg), identical with the product obtained under *b*), and 19β,28-epoxy-25(10→2ξ)*abeo*-A(1)-nor-18α-oleana-5(10),9(11)-diene (*IX*; 40 mg), m.p. 205–207°C (chloroform–methanol); $[\alpha]_D$ +99°. IR spectrum: 1 031 (C—O), UV spectrum: λ_{max}, nm (log ε): 255 (4·18), 246 (4·37), 238 (4·33), 230 (4·18). Mass spectrum, *m/z* (%): 408 (M^+, 42), 393 (100), 377 (14), 363 (3), 347 (2), 337 (2), 187 (15), 173 (40). For $C_{29}H_{44}O$ (408·7) calculated: 85·23% C, 10·85% H; found: 85·35% C, 10·64% H.

b) *With perchloric acid.* Water (1·4 ml) and 70% perchloric acid (0·7 ml) were added to a solution of epoxide *X* (500 mg) in dioxane (35 ml). After standing at room temperature for 20 h, the mixture was worked up as usual. The residue was dissolved in benzene and chromatographed on silica gel in light petroleum–ether (9 : 1). The chromatography afforded in succession: unidentified non-polar compounds (60 mg), alcohol *XII* (35 mg), a mixture of *XII* and *XIV* (80 mg) and alcohol *XIV* (250 mg). 19β,28-Epoxy-25(10→2β)*abeo*-A(1)-nor-18α-olean-9-en-3α-ol (*XII*)

melted at 236–240°C (chloroform–methanol), $[\alpha]_D$ +52°. IR spectrum: 3 612, 3 420 (OH), 1 030 (C—O). Mass spectrum, *m/z* (%): 426 (M^+, 14), 424 (7), 411 (5), 408 (38), 393 (15), 377 (9), 337 (4), 206 (39), 191 (56), 189 (90), 173 (100). For $C_{29}H_{46}O_2$ (426·7) calculated: 81·63% C, 10·87% H; found: 81·52% C, 10·76% H. 19β,28-Epoxy-25(10→2β)*abeo*-A(1)-nor-18α-olean-5(10)-en-3α-ol (*XIV*), m.p. 271–273°C (chloroform–methanol), $[\alpha]_D$ −9°. IR spectrum: 3 612, 3 430 (OH), 1 030 (C—O). Mass spectrum, *m/z* (%): 426 (M^+, 10), 424 (6), 411 (3), 408 (27), 393 (10), 377 (5), 337 (2), 206 (17), 191 (25), 189 (67), 173 (100). For $C_{29}H_{46}O_2$ (426·7) calculated: 81·63% C, 10·87% H; found: 81·41% C, 10·59% H.

c) *With acetic acid.* A solution of epoxide *X* (200 mg) in acetic acid (30 ml) was refluxed for 7 h and then worked up in the usual manner. The residue was dissolved in benzene (2 ml), 10% potassium hydroxide solution in ethanol (3 ml) was added and the mixture was refluxed for 30 min. After the usual work-up, the residue (180 mg) contained alcohols *XII* and *XIV* in the ratio of about 1 : 10 (TLC). Repeated chromatography as described under *b*) and crystallization from chloroform–methanol afforded pure *XII* (5 mg) and *XIV* (25 mg), identical with compounds obtained under *b*). The same mixture of alcohols was obtained by performing the reaction with acetic acid at room temperature for 10 days. When the reaction was carried out in acetic acid containing 5% of sodium acetate (at room temperature for 10 days or at reflux for 1 h), both the alcohols were obtained together with the unreacted epoxide *X*.

d) *With boron trifluoride etherate.* A solution of epoxide *X* (500 mg) and freshly distilled boron trifluoride etherate (0·03 ml) in benzene (10 ml) was allowed to stand at room temperature for 1 h and then worked up in the usual manner. The residue was chromatographed as described sub *b*) and crystallized from chloroform–methanol to give *XI* (60 mg), *XII* (21 mg) and *XIV* (265 mg). 19β,28-Epoxy-25(10→2α)*abeo*-A(1)-nor-10α,18α-oleanan-3-one (*XI*) melted at 224 to 226°C; $[\alpha]_D$ +16°. IR spectrum: 1 729 (C=O), 1 032 (C—O). Mass spectrum, *m/z* (%): 426 (M^+, 44), 411 (8), 418 (6), 395 (11), 355 (100), 220 (21), 205 (45), 191 (51), 149 (45). For $C_{29}H_{46}O_2$ (426·7) calculated: 81·63% C, 10·87% H; found: 81·33% C, 10·70% H.

When the reaction was performed in boiling benzene (3 h), the ketone *XI* was obtained in a 20% yield, the remaining material being a mixture of unidentified dienes (according to mass and UV spectra). Attempted preparation of the enol acetate by treatment of ketone *XI* with isopropenyl acetate in the presence of *p*-toluenesulfonic acid (reflux for 2 days) or the enol ether by reaction with ethyl orthoformate and sulfuric acid (reflux in benzene–ethanol for 1 day) was unsuccessful: in both cases the ketone *XI* was recovered from the reaction mixtures.

19β,28-Epoxy-25(10→2α)*abeo*-A(1)-nor-10α,18α-oleanan-3α-ol (*XVI*)

A mixture of ketone *XI* (50 mg), sodium borohydride (70 mg), benzene (2·5 ml) and ethanol (5 ml) was set aside for 20 h at room temperature and worked up as usual. Crystallization of the residue from chloroform–methanol afforded alcohol *XVI* (38 mg), m.p. 258–260°C; $[\alpha]_D$ +26°. IR spectrum: 3 615, 3 435 (OH); 1 030, 1 047 (C—O). Mass spectrum, *m/z* (%): 428 (M^+, 43), 410 (89), 395 (26), 357 (66), 190 (50), 175 (64), 149 (62), 95 (100). For $C_{29}H_{48}O_2$ (428·7) calculated: 81·25% C, 11·29% H; found: 81·12% C, 11·08% H.

9α,10α;19β,28-Diepoxy-25(10→2β)*abeo*-A(1)-nor-18α-oleanan-3α-ol (*XVIII*)

Reaction of alcohol *XII* (10·6 mg) with 3-chloroperoxybenzoic acid (8·6 mg) was performed as described for *XIX*, affording *XVIII* (5·6 mg), m.p. 247–250°C (chloroform–methanol). IR spectrum: 3 610, 3 440 (OH); 1 031 (C—O). Mass spectrum, *m/z* (%): 442 (M^+, 5), 424 (21), 409 (16), 406 (10), 393 (14), 371 (5), 288 (7), 273 (7), 257 (10), 245 (15), 57 (100).

5α,10α;19β,28-Diepoxy-25(10→2β)*abeo*-A(1)-nor-18α-oleanan-3α-ol (*XIX*)

A solution of alcohol *XIV* (35 mg) and 3-chloroperoxybenzoic acid (32 mg) in chloroform (2 ml) was allowed to stand at 0°C for 20 h, diluted with ether and washed successively with 5% potassium iodide solution, 5% sodium sulfite solution and then processed in the usual manner. Crystallization from chloroform–methanol gave 28 mg of compound *XIX*, m.p. 305–308°C, $[\alpha]_D$ −1°. IR spectrum: 3 530, 3 435 (OH); 1 081, 1 032, 1 005 (C—O). Mass spectrum, *m/z* (%): 442 (M^+, 7), 427 (8), 424 (13), 409 (10), 393 (9), 385 (11), 371 (8), 57 (100). For $C_{29}H_{46}O_3$ (442·7) calculated: 78·68% C, 10·47% H; found: 78·49% C, 10·31% H.

5α,10α;19β,28-Diepoxy-25(10→2β)*abeo*-A(1)-nor-18α-oleanan-3-one (*XX*)

A mixture of epoxy alcohol *XIX* (63 mg), sodium dichromate dihydrate (120 mg), sodium acetate (90 mg) and acetic acid (25 ml) was stirred at room temperature for 20 h. The excess reagent was destroyed with methanol (2 ml) and the mixture was worked up in the usual manner. Crystallization from chloroform–methanol afforded ketone *XX* (49 mg), m.p. 249–252°C, $[\alpha]_D$ +5. ° IR spectrum: 1 742 (C=O); 1 031 (C—O). Mass spectrum, *m/z* (%): 440 (M^+, 28), 425 (26), 422 (35), 412 (18), 409 (15), 407 (16), 391 (18), 384 (44), 369 (93), 353 (17), 351 (16), 245 (29), 203 (41), 95 (100). For $C_{29}H_{44}O_3$ (440·7) calculated: 79·04% C, 10·06% H; found: 78·89% C, 9·89% H. The same procedure furnished ketone *XX* as the only product from alcohol *XIV*.

5α,10α;19β,28-Diepoxy-25(10→2β)*abeo*-A(1)-nor-18α-oleanan-3β-ol (*XXI*)

A suspension of sodium borohydride (84 mg) in ethanol (3·6 ml) was added to a solution of ketone *XX* (50 mg) in benzene (1·5 ml) and ethanol (2·4 ml). After standing at room temperature for 24 h, the mixture was diluted with water and extracted with ether. The ethereal extract was washed five times with water and dried over sodium sulfate. Evaporation of the solvent afforded crystalline alcohol *XXI* (45 mg) which contained only traces of the isomer *XIX* (TLC); m.p. 286–289°C with decomposition to dienol *XXIII* and two unidentified compounds (TLC); $[\alpha]_D$ +16°. Mass spectrum, *m/z* (%): 442 (M^+, 17), 427 (19), 424 (53), 409 (38), 385 (13), 371 (47), 343 (35), 203 (42), 95 (100). For $C_{29}H_{46}O_3$ (442·7) calculated: 78·68% C, 10·47% H; found: 78·39% C, 10·25% H.

19β,28-Epoxy-25(10→2β)*abeo*-A(1)-nor-18α-oleana-5(10),9(11)-dien-3β-ol (*XXIII*)

Ketone *XX* (60 mg) was reduced as described in the preparation of *XXI*. The reaction mixture was diluted with water and ether, acidified with 10% hydrochloric acid, the ethereal layer was washed with 10% hydrochloric acid and further processed as usual. Chromatography on silica gel in light petroleum–ether (9 : 1) and crystallization from chloroform–methanol afforded dienol *XXIII* (43 mg), m.p. 294–296°C; $[\alpha]_D$ +89°. IR spectrum: 3 613, 3 435 (OH); 1 031 (C—O). UV spectrum: λ_{max}, nm (log ε): 255 (4·05), 246 (4·24) 238 (4·20), 230 (4·06). Mass spectrum, *m/z* (%): 424 (M^+, 100), 409 (80), 406 (11), 393 (44), 379 (14), 375 (14), 353 (7), 203 (33), 189 (52), 187 (29). For $C_{29}H_{44}O_2$ (424·7) calculated: 82·02% C, 10·44% H; found: 81·87% C, 10·30% H.

Dienol *XXIII* was obtained in attempts to purify alcohol *XXI* by chromatography on silica gel, on crystallization from chloroform–methanol or on standing of its chloroform solutions. Shaking a solution of *XXI* (1 mg) in a mixture of benzene (0·5 ml) and ethanol (0·5 ml) with 10% hydrochloric acid (1 ml) gave about 50% of *XXIII* after 10 min; after 1 h the mixture contained solely *XXIII*. Ketone *XX* and alcohol *XIX* did not react under the same conditions.

19β,28-Epoxy-25(10→2β)*abeo*-A(1)-nor-18α-olean-5(10)-ene (*XXVI*) and 19β,28-Epoxy-25(10→2β)*abeo*-A(1)-nor-18α-olean-9-ene (*XXVII*)

Olefin *VIII* (50 mg) in 98% formic acid (5 ml) was refluxed for 5 h. After the usual work-up procedure the residue was dissolved in cyclohexane and filtered through alumina (5 g; neutral, activity II); yield 43 mg of a 1 : 1 mixture (^{1}H and ^{13}C NMR) of *XXVI* and *XXVII*, unseparable by TLC. The components were separated by HPLC and the purest fractions were crystallized from ether–methanol, yielding *XXVI* (3 mg; m.p. 193–196°C) and *XXVII* (4 mg; m.p. 143 to 150°C).

A(1)-Nor-18α-olean-2-en-28→19β-olide (*XXVIII*)

Ketone *I*, contaminated with 3-oxo-18α-oleanan-28→19β-olide, was converted into olefin *VIII* using the reaction sequence described in ref.[1] (*I* → *II* → *III* → *IV* → (*V* + *VI*) → *VIII*). The obtained olefin *VIII* contained lactone *XXVIII* which was isolated by chromatography on silica gel in light petroleum–ether (9 : 1); m.p. 334–336°C (chloroform–methanol); $[\alpha]_D$ +62°. IR spectrum: 1 762 (C=O); 1 153, 1 122, 971 (C—O). ^{1}H NMR spectrum (80 MHz): 0·90 s, 3 H; 0·92 s, 3 H; 0·93 s, 3 H; 0·96 s, 3 H; 0·97 s, 3 H and 1·03 s, 6 H (7 × CH_3); 3·93 s, 1 H (H-19); 5·47 d, 1 H and 5·97 d, 1 H (H-2 and H-3, J(2, 3) = 5·7). Mass spectrum, m/z (%): 424 (M^+, 21), 409 (100), 203 (14), 189 (35), 175 (77), 173 (33), 121 (90), 109 (76), 107 (94). For $C_{29}H_{44}O_2$ (424·7) calculated: 82·02% C, 10·44% H; found: 81·98% C, 10·21% H.

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