ANHYDROBETULIN AND ITS DERIVATIVES*

Alois VYSTRČIL[a], Václav KŘEČEK[a], Jiří PROTIVA[a] and Miloš BUDĚŠÍNSKÝ[b]

[a] *Department of Organic Chemistry, Charles University, 128 40 Prague 2*

[b] *Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6*

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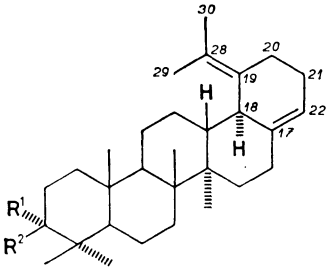
The structure of anhydrobetulin *II* and its derivatives *I*, *III* and *IV* has been solved using ^{1}H and ^{13}C NMR spectra, mass spectra and chemical transformations. It has been proven that in addition reactions the trisubstituted double bond is attacked selectively from the α-side under formation of D/E *cis*-annelated derivatives *VIII*, *X* and *XI*. The 22-oxo derivative *XIII* exhibits an anomalous Cotton effect and, in contrast to its saturated analogue *XXVII*, it is not epimerized in alkaline medium. Trinordiketone *XXI* easily epimerizes to a mixture in which the 17βH-epimer *XXIb* predominates, trinorketone *XXIV* is stable only if the annelation of rings D and E is *trans*. These differences are explained in terms of steric interactions of substituents in position 19. The steric course of reduction of ketones *XIII* and *XXIV* with sodium borohydride is described.

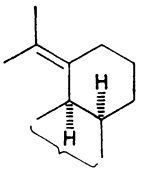
In our previous communication[1] we suggested the structure of anhydrobetulin *II* and its derivatives *I*, *III* and *IV* prepared by solvolysis of lup-20(29)-en-28-yl *p*-toluenesulfonate derivatives or the corresponding 17,22-dihydroderivatives *V*–*VII*. To provide further confirmation of the proposed structures we measured their ^{1}H, ^{13}C NMR and mass spectra and performed further chemical transformations.

The ^{1}H NMR spectra (Table I) of dienes *I*–*IV* exhibit a characteristic signal of a doubly allylic proton H-18 as a broad dublet at δ 2·90 with coupling constant J(18, 13) of about 11 Hz, indicative of trans arrangement of the H-18 and H-13 protons. This means that in the preparation of anhydro derivatives *I*–*IV* the configuration on C-18 remains unchanged and that both the double bonds are homoconjugated. The signal of the vinyl proton H-22 also appears as a broadened doublet (δ 5·34) whose coupling constants (5·0 and <1 Hz) correspond approximately to the torsion angles Φ (H-22, H-21β) $\approx$ 50° and Φ (H-22, H-21α) $\approx$ 75° (for determination of torsion angles see the NMR discussion). As seen on models, these values are compatible with a flattened half-boat conformation of the ring E in which the methyl group (29-Me) of the isopropylidene side chain assumes a maximum distance from the C(12) methylene group. From the coupling constants J(18, 13) $\approx$ 11·7 Hz

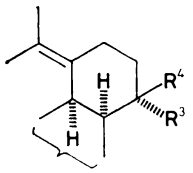
* Part XCIII in the series Triterpenes; Part XCII: Collect. Czech. Chem. Commun. *55*, 766 (1990).



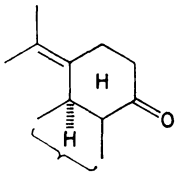
I, $R^1 = R^2 = H$
II, $R^1 = H$; $R^2 = OH$
III, $R^1 = H$; $R^2 = OAc$
IV, $R^1 + R^2 = O$



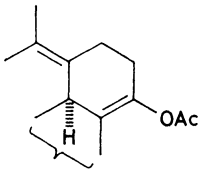
V, $R^1 = H$; $R^2 = OH$
VI, $R^1 = H$; $R^2 = OAc$
VII, $R^1 + R^2 = O$



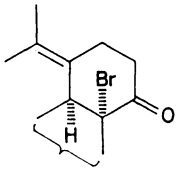
VIII, $R^1 = R^2 = R^4 = H$; $R^3 = OH$
IX, $R^1 = R^2 = R^4 = H$; $R^3 = OAc$
X, $R^1 = R^4 = H$; $R^2 = R^3 = OH$
XI, $R^1 = R^4 = H$; $R^2 = OAc$; $R^3 = OH$
XII, $R^1 = R^4 = H$; $R^2 = R^3 = OAc$
XXIX, $R^1 = R^2 = R^3 = H$; $R^4 = OH$
XXX, $R^1 = R^2 = R^3 = H$; $R^4 = OAc$



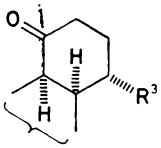
XIII, $R^1 = R^2 = H$
XIV, $R^1 = H$; $R^2 = OH$
XV, $R^1 = H$; $R^2 = OAc$
XVI, $R^1 + R^2 = O$



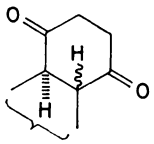
XVII, $R^1 = R^2 = H$



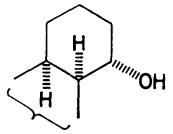
XVIII, $R^1 = R^2 = H$



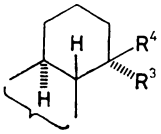
XIX, $R^1 = R^2 = H$; $R^3 = OH$
XX, $R^1 = R^2 = H$; $R^3 = OAc$
XXII, $R^1 = R^2 = R^3 = H$



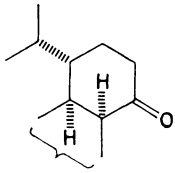
XXIa, $R^1 = R^2 = H$; 17α-H
XXIb, $R^1 = R^2 = H$; 17β-H



XXIII, $R^1 = R^2 = H$

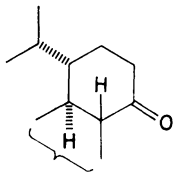


XXIV, $R^1 = R^2 = H$; $R^3 + R^4 = O$
XXV, $R^1 = R^2 = R^4 = H$; $R^3 = OH$
XXVI, $R^1 = R^2 = R^3 = H$; $R^4 = OH$



XXVII

$R^1 = R^2 = H$



XXVIII

TABLE I

Proton NMR data of compounds *I*—*XVII*, *XIX*—*XXI*, *XXIII*—*XXX* in deuterochloroform; for other conditions see Experimental

Compound	Freq.	Methyl protons[a]							Other protons
		H-23	H-24	H-25	H-26	H-27	H-29[b]	H-30[b]	
I	200	0·851	0·792	0·824 (0·7)	0·957	1·127 (0·6)	1·688	1·641 (1·3)	H-18: 2·90 bd, J(18, 13) = 11·1; H-22: 5·34 bd, J(22, 21) = 5 and <1
II	200	0·977	0·761	0·829	0·955	1·117	1·688	1·637 (1·2)	H-3: 3·21 m; H-18: 2·90 bd, J(18, 13) = 11·0; H-22: 5·34 bd, J(22, 21) = 5 and <1
III	200	0·845	0·845	0·835	0·955	1·114	1·688	1·643	H-3: 4·49 m; OAc: 2·04 s; H-18: 2·90 bd, J(18, 13) = 11·1; H-22: 5·34 bd, J(22, 21) = 5 and <1
IV	200	1·084	1·026	0·926 (0·9)	0·994	1·131	1·694	1·641 (1·3)	H-2α: 2·41 ddd, J(2α, 1α) = 8·0, J(2α, 1β) = 4·9, J(2α, 2β) = 15·7; H-2β: 2·51 ddd, J(2β, 1α) = 9·4, J(2β, 1β) = 7·2, J(2β, 2α) = 15·7; H-18: 2·92 bd, J(18, 13) = 11·1; H-22: 5·35 bd, J(22, 21) = 5 and <1
V	200	0·971	0·764	0·838 (0·7)	1·026	0·993	1·643	1·621	H-3: 3·20 m; H-13: 1·91 dt, J((13, 18) = 11·7, J(13, 12) = 12·3 and 3·4; H-18: 2·65 dd, J(18, 13) = 11·7, J(18, 17) = 4·3; H-20α: 2·42 m
VI	200	0·850	0·838	0·864	1·026	0·998	1·644	1·626	H-3: 4·48 m; OAc: 2·04 s; H-13: 1·91 ddd, J(13, 18) = 11·5, J(13, 12) = 12·5 and 3·5; H-18: 2·65 dd, J(18, 13) = 11·5, J(18, 17) = 4·4; H-20α: 2·43 m
VII	200	1·078	1·029	0·935 (0·8)	1·064	1·004	1·648	1·624	H-2α, H-2β and H-20α: 2·45 m; H-18: 2·67 dd, J(18, 13) = 11·7, J(18, 17) = 4·3

VIII	200	0·847	0·793	0·827 (0·7)	1·027	1·009	1·662 (1·1)	1·631 (1·7)	H-18: 2·76 bdd, $J(18, 13) = 11·8$, $J(18, 17) = 4·7$; H-20α: 2·52 m, $J(20\alpha, 20\beta) = 14·0$, $J(20\alpha, 21) = 3·8$ and 3·2; H-21β: 2·06 m, $J(21\beta, 20) = 3·2$ and 3·5, $J(21\beta, 21\alpha) = 11·5$, $J(21\beta, 22) = 4·7$; H-22: 3·99 dt, $J(22, 17) \approx J(22, 21\alpha) \approx 10·8$, $J(22, 21\beta) = 4·7$
IX	200	0·844	0·797	0·832	1·047	1·012	1·661 (1·0)	1·636 (1·7)	H-18: 2·79 bdd, $J(18, 13) = 11·7$, $J(18, 17) = 4·4$; OAc: 2·02 s; H-20α: 2·52 bdt, $J(20\alpha, 20\beta) = 14·2$; $J(20\alpha, 21) = 3·5$ and 3·5; H-22: 5·26 dt, $J(22, 17) \approx J(22, 21\alpha) \approx 11·0$, $J(22, 21\beta) = 4·8$
X	60	0·97	0·76	0·83	1·00—1·02		1·63—1·65		
XI	60	0·83—0·86	0·83—0·86	0·83—0·86	1·01	1·1	1·64—1·66		H-3: 4·47 m; OAc: 2·03 s
XII	500	0·846	0·838	0·858	1·042	0·995	1·663	1·640 (1·5)	H-3: 4·47 m; OAc: 2·03 s, 2·04 s; H-18: 2·79 dd, $J(18, 17) = 4·5$, $J(18, 13) = 11·8$; H-20α: 2·52 bdt, $J(20\alpha, 20\beta) = 14·4$, $J(20\alpha, 21) = 3·5$ and 3·5; H-22: 5·25 dt, $J(22, 17) \approx J(22, 21\alpha) \approx 11·2$, $J(22, 21\beta) = 4·9$
XIII	360	0·840	0·783	0·807 (0·7)	0·911	0·998 (0·7)	1·748 (0·8)	1·738 (1·6)	H-18: 3·08 ddd, $J(18, 13) = 11·6$, $J(18, 17) = 5·5$, $J(18, 20\alpha) = 1·7$
XIV	60	0·96—0·98	0·75	0·80	0·90	0·96—0·98	1·74	1·74	H-3: 3·20 m
XV	60	0·83—0·86	0·83—0·86	0·83—0·86	0·92	0·98	1·75	1·75	H-3: 4·48 m; OAc: 2·03 s
XVI	60	1·07	1·00—1·02	0·94	0·91	1·00—1·02	1·74—1·76	1·74—1·76	

TABLE I
(*Continued*)

Compound	Freq.	Methyl protons[a]							Other protons
		H-23	H-24	H-25	H-26	H-27	H-29[b]	H-30[b]	
XVII	100	0·837	0·781	0·814	0·952	1·093	1·667	1·624	H-18: 2·98 bd, $J(18, 13) = 11$; OAc: 2·07 s
XIX	60	0·84—0·86	0·81	0·84—0·86	1·07	0·96	—	—	H-22: 4·15 m
XX	100	0·847	0·801	0·847	1·100	0·946	—	—	H-22: 5·47 dt, $J(22, 17) \approx J(22, 21\alpha) \approx 11{\cdot}5$, $J(22, 21\beta) = 4{\cdot}2$; OAc: 2·04 s
XXIa	200	0·841	0·787	0·818 (0·6)	0·949	0·934 (0·7)	—	—	
XXIb	200	0·841	0·797	0·859 (0·8)	1·012	0·900	—	—	
XXIII	200	0·844	0·796	0·844	1·005	0·955	—	—	H-22: 3·85 dt, $J(22, 17) \approx J(22, 21\alpha) \approx 10{\cdot}6$, $J(22, 21\beta) = 4{\cdot}8$
XXIV	200	0·844	0·797	0·844	0·977	0·884	—	—	
XXV	200	0·845	0·798	0·845	0·969	0·932	—	—	H-22: 3·72 q, $J(22, 17) \approx J(22, 21\alpha) \approx J(22, 21\beta) \approx 2{\cdot}7$
XXVI	200	0·846	0·800	0·842	0·968	0·915	—	—	H-22: 3·49 dt, $J(22, 17) \approx J(22, 21\beta) \approx 9{\cdot}6$, $J(22, 21\alpha) = 4{\cdot}6$

XXVII	100	0·840	0·789	0·819	0·894	0·937	0·96 (6·5)	0·96 (6·5)	
XXVIII	100	0·852	0·800	0·852	0·998	0·925	0·833 (6·5)	0·893 (6·5)	
XXIX	360	0·844	0·789	0·824	1·005	1·020	1·673 (1·0)	1·627 (1·7)	H-13: 2·19 ddd, J(13, 12) = 12·5 and 3·6, J(13, 18) = 11·8; H-18: 2·66 dd, J(18, 13) = 11·8, J(18, 17) = 5·5; H-20α: 2·32 dt, J(20α, 20β) = 13·6, J(20α, 21) = 3·6 and 3·6; H-20β: 2·09 dt, J(20β, 20α) = 13·6, J(20β, 21β) = 4·9, J(20β, 21α) = 13·1; H-21β: 1·76 dq, J(21β, 21α) = 13·4, J(21β, 20α) ≈ J(21β, 20β) ≈ J(21β, 22) ≈ 3·2; H-22: 3·99 q, J(22, 17) ≈ J(22, 21α) ≈ J(22, 21β) ≈ 3·1
XXX	200	0·851	0·795	0·851	1·072	1·021	1·669	1·638	H-13: 2·13 dt, J(13, 12) = 12·5 and 3·5, J(13, 18) = 11·9; H-18: 2·73 dd, J(18, 13) = 11·9, J(18, 17) = 5·3; OAc: 2·12 s; H-20α: 2·32 dt, J(20α, 20β) = 13·8, J(20α, 21) = 3·5 and 3·5; H-22: 5·07 q, J(22, 17) ≈ J(22, 21α) ≈ J(22, 21β) ≈ 3·0

[a] Singlets; in some cases a fine splitting due to the long-range coupling was observed (J value given in parentheses); [b] the signals may be interchanged.

and $J(18, 17) \approx 4{\cdot}4$ Hz in the ^{1}H NMR spectra of the dihydro derivatives *V–VII* (Table I) we can derive approximate values of the torsion angles Φ(H-18, H-13) $\approx$ $\approx 170°$ and Φ(H-18, H-17) $\approx 50°$, compatible with *cis*-fusion of rings D and E. Thus, the addition of hydrogen to the trisubstituted double bond of dienes *I* and *III* took place from the α-side, similarly as in the previously described[2] hydrogenation of anhydro derivatives with isopropyl side chain.

^{13}C NMR spectra of dienes *I–IV* and 17,22-dihydro derivatives *V* and *VII* (Table II) are in accord with the proposed structures. Reduction of the 17,22-double bond results – besides dramatic upfield shifts of C-17 and C-22 signals due to change of hybridization – also in smaller shifts of carbon signals in the α- and β-position to the reduced double bond (upfield shifts of C-13, C-16, C-18, C-20 and C-21 and downfield shifts of C-15 and C-19 signals).

Another confirmation of the suggested structures is the conversion of anyhdro derivatives *I–III* by reaction with diborane and subsequent oxidation (H_2O_2, NaOH) to hydroxy derivatives *VIII*, *X* and *XI* which were further characterized as the acetyl derivatives *IX* and *XII*.

As follows from the ^{1}H and ^{13}C NMR spectra of the hydroxy derivatives *VIII*, *X* or the acetate *IX*, the addition of diborane to dienes *I–III* left the exocyclic double bond intact (signals of methyl groups on the double bond at δ 1·66 and 1·63 in ^{1}H NMR spectrum and olefinic carbon signals $>$C= at δ 132 and 123 in ^{13}C NMR spectrum). The coupling constants in the spectrum of hydroxy derivative *VIII* and its acetate *IX* show that the D/E ring fusion is *cis* ($J(18,17) \approx 4{\cdot}5$ Hz) and that the ring E exists in a chair conformation (Φ(H-22β, H-17α) $\approx 170°$, Φ(H-22β, H-21α) $\approx$ $\approx 170°$, Φ(H-22β, H-21β) $\approx 50°$, Φ(H-21β, H-20α) $\approx$ Φ(H-21α, H-20α) $\approx 55°$).

The hydroxy derivative *VIII* was oxidized to ketone *XIII*; in the same manner the hydroxy derivative *XI* was converted into ketone *XV* which was hydrolyzed to hydroxy ketone *XIV* and this oxidized to diketone *XVI*. The 17αH-configuration of the starting 22-hydroxy derivatives *VIII* and *X*, as well as the analogy with the previously described[2] ketone *XXVII* containing the 19α-isopropyl side chain, led us to the assumption that also in the 22-oxo derivatives *XIII–XVI* the D/E annelation is *cis*. The 17αH-configuration in ketone *XIII* was proven by the ^{1}H NMR spectrum (360 MHz) in which the H-18 signal appeared at δ 3·08 (ddd) with coupling constants $J(18, 17) = 5{\cdot}5$, $J(18, 13) = 11{\cdot}6$ and $J(18, 20\alpha) = 1{\cdot}7$ Hz. The *cis* ring fusion was confirmed also by the ^{13}C NMR signals.

On the other hand, the Cotton effect (CD : $\Delta\varepsilon = -1{\cdot}14$ (305 nm) and $-1{\cdot}09$ (295 nm)) indicates a rather opposite configuration at C(17), as also would be suggested by the resistance of ketone *XIII* to equilibration under conditions[2] causing equilibration of ketone *XXVII* to an 88 : 12 mixture with its epimer *XXVIII*. This discrepancy between the NMR results on the one hand and the CD and equilibration data on the other are probably related to the conformational change of the ketone *XIII* with the given configuration 17αH, 18αH.

Therefore we decided to introduce such substituent into position 17α which would decisively determine the sense of the Cotton effect regardless of the possible conformational changes of the ring E. Acid-catalyzed reaction of ketone *XIII* with isopropenyl acetate afforded only one enol acetate (see ref.[3]) which we assign the structure *XVII* (IR spectrum: 1 748, 1 711 cm^{-1}; ^1H NMR spectrum: δ 1·62 bs, 3 H and 1·67 bs, 3 H) with the original configuration 18αH (δ 2·98 bd, H-18, $J(18, 13)$ = = 11 Hz). By reaction of the enol acetate *XVII* with bromine in acetic acid and pyridine we obtained only one bromo ketone *XVIII* (see ref.[3]) with a marked negative Cotton effect (CD : $\Delta\varepsilon = -2{\cdot}02$ (293 nm)), i.e. with *cis*-fused rings D and E.

In order to explain the different behaviour of 17αH-ketones *XIII* and *XXVII* under the equilibration conditions we tried to prepare 22-oxo derivatives containing less bulky or no substituents in position C(19). Ozonolysis of acetate *IX* afforded trinor ketone *XX* with retained configuration 17αH ($J(17, 22)$ = 11·5 Hz) whose ORD curve was analogous to that of the previously described[1] deoxy ketone *XXII*. Compound *XX* underwent basic hydrolysis to give hydroxy ketone *XIX*; this was oxidized to diketone *XXI* which was shown (^1H and ^{13}C NMR spectra) to be an unseparable mixture of the 17-epimers. As judged from the relative intensities of methyl signals (H-26 : δ 0·949 and 1·012; H-27: δ 0·934 and 0·900) and signals of C-17 and C-18 carbon atoms (C-17 : δ 54·00 and 51·16; C-18 : δ 51·56 and 47·70), the isolated mixture of epimers contained only minor amounts of the 17α-ketone *XXIa*. The facile epimerization of diketone *XXI* is also illustrated by the changes of the ORD curves in 0·1M hydrochoric acid in dioxane at room temperature during 24 hours.

The mass spectra of compounds *XIX*–*XXI* exhibit no marked features. Besides the molecular ion, the only abundant ions are those at m/z 191, ascribed to the rings A and B.

The 19-oxo group was removed by the Wolff–Kishner reduction of compound *XX*; in the obtained alcohol *XXIII* the *cis*-annelation of the rings D/E is preserved ($J(22, 17)$ = 10·6 Hz). The subsequent oxidation of *XXIII* afforded uniform ketone *XXIV* with a negative Cotton effect. The compound was not equilibrated in an alkaline medium and according to chemical shifts of the 26- and 27-methyl protons (δ 0·977 and 0·884, respectively) has the 17βH-configuration. The final proof of its D/E *trans*-annelation has been obtained by its reduction to alcohols *XXV* and *XXVI*.

The effect of substituents in the position C(19) on the epimerization of 17αH,22-oxo derivatives can be summarized as follows: the epimerization is completely suppressed by 19-isopropylidene group, partly suppressed by 19α-isopropyl group and even less by 19-oxo group, and finally, 19-unsubstituted 22-oxo derivatives are stable only when the D/E annelation is *trans*.

Reduction of ketone *XXIV* with sodium borohydride afforded a mixture of epimeric alcohols *XXV* ($J(22, 17) \approx J(22, 21\alpha) \approx J(22, 21\beta) \approx 2{\cdot}7$ Hz) and *XXVI* ($J(22, 17) \approx J(22, 21\beta) = 9{\cdot}6$ Hz, $J(22, 21\alpha) = 4{\cdot}6$ Hz) in which the equatorial alcohol *XXVI*

TABLE II

Carbon-13 chemical shifts of compounds *I*—*IX*, *XII*, *XIII*, *XXI*, *XXIII*—*XXV*; for other condi-

Carbon	*I*	*II*	*III*[a]	*IV*	*V*	*VI*[b]	*VII*	*VIII*
C-1	40·43	38·47	38·51	39·73	38·80	38·47	39·71	40·35
C-2	18·72	26·80	23·68	34·40	27·42	23·71	34·14	18·70
C-3	42·11	78·59	80·90	218·13	79·09	80·97	218·27	42·11
C-4	33·28	38·62	37·78	47·28	38·88	37·80	47·32	33·27
C-5	56·49	55·28	55·45	54·90	55·41	55·48	54·96	56·50
C-6	18·62	18·10	18·16	19·65	18·31	18·19	19·70	18·60
C-7	34·46	34·30	34·44	33·41	33·90	33·83	33·18	33·81
C-8	41·29	40·89	41·07	40·97	41·07	41·07	40·99	41·31
C-9	51·06	50·83	50·87	50·29	50·98	50·88	50·32	51·01
C-10	37·51	36·99	37·09	36·89	37·22	37·12	36·93	37·50
C-11	21·16	21·08	21·26	21·80	21·39	21·39	21·94	21·16
C-12	25·82	25·53	25·67	25·69	25·92	25·90	25·91	25·70
C-13	42·24	42·03	42·15	42·09	33·90	33·87	34·01	35·57
C-14	42·24	42·03	42·20	42·26	41·72	41·70	41·79	41·50
C-15	23·92	23·68	23·89	23·89	25·12	25·09	25·12	25·25
C-16	34·13	34·01	34·08	34·09	27·96	27·94	27·91	21·91
C-17	143·55	143·22	143·36	143·19	37·53	37·51	37·47	44·28
C-18	44·75	44·61	44·69	44·77	40·21	40·18	40·14	40·47
C-19	130·63	130·42	130·46	130·41	133·93	133·85	133·78	132·15
C-20	27·33	27·06	27·29	27·28	27·59	27·59	27·56	24·10
C-21	32·25	32·09	32·28	32·23	26·41	26·41	26·43	36·61
C-22	117·25	117·12	117·35	117·51	25·12	25·09	25·12	67·15
C-23	33·37	27·65	27·92	26·72	27·99	27·94	26·73	33·37
C-24	21·55	15·11	16·48	21·02	15·39	16·50	21·02	21·54
C-25	16·34	16·07	16·40	16·20	16·34	16·40	16·20	16·30
C-26	15·98	15·67	15·89	15·71	15·84	15·82	15·66	15·86
C-27	14·96	14·67	14·88	14·83	14·28	14·24	14·20	14·51
C-28	123·36	123·14	123·48	123·56	121·73	121·79	121·90	123·56
C-29[e]	21·05	21·08	21·04	20·98	20·43	20·44	20·43	20·98
C-30[e]	19·86	19·51	19·84	19·85	20·26	20·25	20·27	20·31

[a] OAc: 170·95 (C=O), 21·30 (CH_3); [b] OAc: 170·99 (C=O), 21·33 (CH_3); [c] OAc: 170·92 (C=O),

predominated. On the contrary, reduction of ketone *XIII* under the same conditions furnished alcohol *XXIX* as the principal product. According to the ^{1}H NMR spectrum, this product has clearly axial hydroxyl ($J(22, 21\alpha) \approx J(22, 21\beta) \approx 3{\cdot}1$ Hz), the original configuration 13βH ($J(13, 12\alpha) = 12{\cdot}5$ Hz and $J(13, 12\beta) = 3{\cdot}6$ Hz), 18αH ($J(18, 13) = 11{\cdot}8$ Hz) and 17αH ($J(17, 18) = 5{\cdot}5$ Hz being preserved. As follows further from the coupling constants $J(20\alpha, 21\beta) \approx J(20\alpha, 21\alpha) = 3{\cdot}6$ Hz and

TABLE II
tions see Experimental

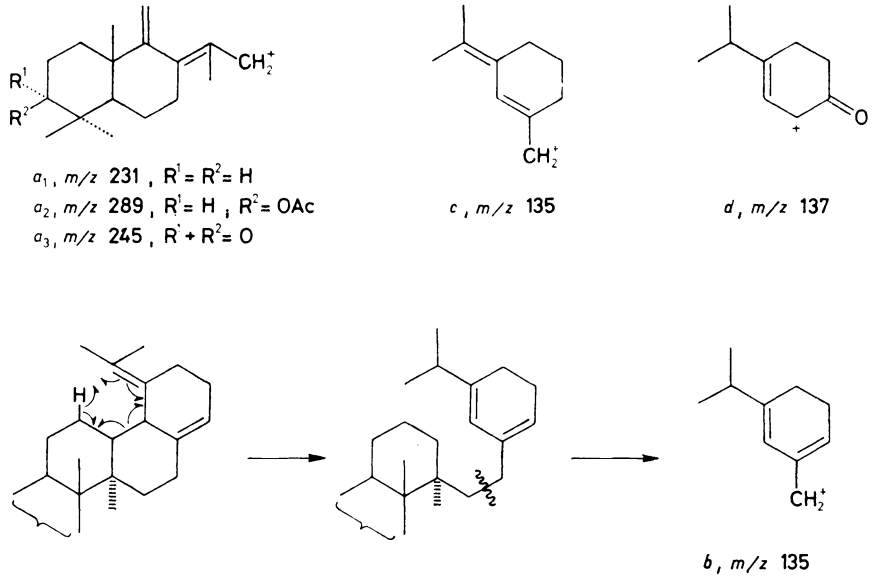
IX[c]	*XII*[d]	*XIII*	*XXIa*	*XXIb*	*XXIII*	*XXIV*	*XXV*
40·35	38·46	40·37	40·26	40·41	40·33	40·38	40·41
18·70	23·68	18·70	18·59	18·66	18·68	18·67	18·71
42·13	80·95	42·11	41·99	42·08	42·10	42·06	42·12
33·26	37·80	33·27	33·28	33·25	33·26	33·25	33·28
56·50	55·49	56·47	56·34	56·56	56·42	56·43	56·50
18·58	18·14	18·57	18·47	18·53	18·61	18·55	18·61
33·72	33·69	33·83	33·70	33·70	33·84	33·83	33·91
41·23	41·04	41·15	41·12	40·99	41·13	40·76	40·79
50·97	50·80	50·79	50·38	50·82	50·46	50·42	50·66
37·48	37·09	37·48	37·44	37·52	37·45	37·44	37·48
21·09	21·21	20·91	21·44	20·75	20·92	20·86	20·95
25·83	25·86	25·09	26·60	29·44	24·97	25·64	25·14
35·39	35·40	38·14	38·10	37·09	36·78	44·13	43·25
41·43	41·41	41·26	39·94	40·92	41·39	40·80	41·27
25·18	25·06	25·16	26·16	26·42	25·63	26·52	25·52
22·16	22·12	20·76	20·50	19·82	21·75	20·70	20·19
41·59	41·54	49·77	54·00	51·16	44·66	55·17	47·11
40·42	40·38	42·17	51·56	47·70	33·58	41·51	35·01
131·48	131·35	129·86	208·34	208·82	27·60	29·55	30·27
23·68	23·68	27·08	36·55	38·07	19·84	29·84	31·05
32·62	32·61	41·58	38·29	38·64	36·41	44·62	33·40
70·30	70·27	212·75	210·80	209·30	66·97	214·00	70·94
33·36	27·92	33·37	33·32	33·32	33·36	33·33	33·35
21·54	16·48	21·55	21·48	21·48	21·54	21·52	21·54
16·26	16·35	16·25	16·22	16·40	16·22	16·28	16·32
15·90	15·84	15·78	15·68	15·60	15·79	15·67	15·71
14·48	14·42	14·11	13·71	15·31	14·17	14·68	14·92
123·04	123·58	125·49	—	—	—	—	—
20·63	20·59	20·63	—	—	—	—	—
20·33	20·32	20·55	—	—	—	—	—

21·32 (CH_3); [d] 2 × OAc: 171·02, 170·99 (C=O), 21·32 (2 × CH_3); [e] the signals may be interchanged.

$J(20\beta, 21\alpha) = 13{\cdot}1$, $J(20\beta, 21\beta) = 4{\cdot}9$ Hz, the ring E assumes a chair conformation. Similar conclusions follow from the ^{1}H NMR spectrum of acetate *XXX* (see Table I).

Mass spectra of all derivatives with the 19(28) double bond are very rich. Besides the classical abundant ions belonging to ring A (ref.[4]) – *m/z* 191 and 177 for 3-deoxy derivatives, *m/z* 189 for 3-acetoxy derivatives, *m/z* 207 for 3-hydroxy derivatives

and m/z 205 for 3-oxo derivatives – all the spectra exhibit ions of the type *a* (m/z 229 and 231 for 3-deoxy, m/z 289 for 3-acetoxy and m/z 245 for 3-oxo derivatives) whose formation from oleanane derivatives with double bond in the E ring has already been described[5]. The most significant in all the spectra are ions of m/z 135 ($C_{10}H_{15}$) for compounds without substituent in position 22, compounds with 17(22) double bond, 22-acetoxy derivatives and in part 22-hydroxy derivatives. For 22-oxo and 22-hydroxy derivatives the most abundant are ions of m/z 137 (which in all cases consist of the $C_9H_{13}O$ and $C_{10}H_{17}$ fragments in the ratio 5 : 1). The ion of m/z 135 can arise either by direct cleavage of the ring D or by initiation of the double bond in position 19(28) (Scheme 1). The ion (m/z 135) has then two possible structures



SCHEME 1

– *b* and *c*. The ion at m/z 137 ($C_9H_{13}O$) in the spectra of 22-oxo derivatives has an analogous structure *d*. A more difficult explanation is required for the ions at m/z 137 ($C_9H_{13}O$) arising from the 22-hydroxy derivatives *VIII*, *X*, *XI* and *XXIX*; this, however, would be only speculative without study of deuterated analogues.

NMR DISCUSSION

^{1}H NMR *Spectra*

The signals of the angular methyl groups (H-23, 24 and 25) in the spectra of compounds *I*–*XXX* are affected neither by substituents in the ring E nor by a change

of the D/E ring fusion. To assign them we used a comparison with lupane derivatives (refs[6,7]). The differences between them reflect the substituent effects of 3β-OH, 3β-OAc and 3-oxo functionalities, known for triterpenes with e.g. lupane or oleanane skeleton (refs[7,8] and references therein). More complicated was the assignment of signals of angular methyl groups, H-26 and H-27. In the case of compounds *I–IV*, differing only in substitution in position 3, we made use of the known[7,8] fact, that the effect of the 3-oxo group on H-26 is more pronounced than on H-27 (about +0·04 ppm and +0·01 ppm, respectively[7,8]). The reverse order of signals of H-26 and H-27 is obviously due to the 17(22) double bond, shielding the H-26 and deshielding the H-27 protons. The above-mentioned effect of 3-oxo group was utilized also for the assignment of H-26 and H-27 in the series of compounds *V–VII*. As expected, for derivatives *VIII–X* and *XII* the effect of the 22α-substituent is negligible and the assignement is therefore analogous to that for compounds *V–VII*. In the case of derivatives *XXIX* and *XXX*, containing 22β-OH and 22β-OAc groups, acetylation results in shift of only one methyl signal which, considering the steric proximity, can be ascribed to H-26. For the 22-oxo derivatives *XIII*, *XV* and *XVI* the data available were not determined with comparable accuracy (60 vs 360 MHz). Nevertheless, the observed upfield shift ($\delta \approx 0{\cdot}91$) of only one methyl can be explained by its orientation towards the 22-oxo group and thus this signal was ascribed to H-26. In the enol acetate *XVII* both methyl groups can be assigned in analogy with the diene *I*. For the 22α-substituted ketones *XIX* and *XX* we made use of analogy with the pair of compounds *VIII* and *IX*: the signal that was somewhat more affected by acetylation was assigned H-26. In the case of compound *XXIa* the assignment was enabled by the observed marked upfield shift of the H-26 signal, connected with oxidation of the 22α-OH group (δ 0·949 for *XXIa* compared with δ 1·07 for *XIX*) an effect analogous to that observed for the pair *XIII* and *VIII*. The same reasoning was used in the assignment of compounds *XXVII* and *XXIII*. Signals of H-29 and H-30 methyl protons have not been asigned.

Of the other hydrogen atoms in compounds *I–XXX* it has been possible to identify only some protons in the neighbourhood of substituents and assign them structurally on the basis of chemical shifts and multiplicities. The approximate values of torsion angles mentioned in the discussion, were obtained from the vicinal coupling constants by application of the Karplus-type relation, derived for cyclohexane[9]. For substituents on fragment —CH_2—CH_2— the experimental values, ^3J(exp), were corrected using the known[10] relation $^3J\,(\mathrm{corr}) = {}^3J(\mathrm{exp})/1 - 0{\cdot}1\sum\Delta E(X_i)$, where $\Delta E(X_i)$ is the difference between the Pauling's electronegativity values[11] for the first substituent atom and hydrogen. The torsion angles given in the text correspond to the thus-calculated values, rounded up to 5°.

^{13}C NMR *Spectra*

From the proton-decoupled and "attached proton test" ^{13}C NMR spectra we were

able to classify experimentally the signals belonging to carbon atoms of the type $-CH_3$, $-CH_2-$, $>CH-$ and $>C<$. From the characteristic values of chemical shifts we easily assigned the signals of sp^2 carbon atoms in the C=C and C=O groups and atoms of the type $>CH-O$. Comparison of chemical shifts with those of known lupane derivatives, analogously substituted in the position 3, led to assignment of signals of all angular methyl groups and carbon atoms of rings A, B and C. The carbon atoms C-29 and C-30 of the isopropenyl group have not been structurally assigned. The carbon atoms of rings D and E of the same type ($-CH_2-$, $>CH-$ and $>C<$) were assigned only tentatively on the basis of a detailed comparison within the studied series of compounds, the known substituent effects, particularly in structurally analogous steroidal fragments (ref.[12]), and derivatization shifts (acetylation or oxidation of an OH group etc.). For the mixture of diketones *XXIa* and *XXIb* we made use of chemical shifts of carbon atoms C-17 and C-18 at the sites of D/E fusion in order to distinguish the epimers. The higher shifts (δ 54·00 and 51·56) were ascribed to the *cis*-isomer *XXIa* whereas the lower ones (δ 51·16 and 47·70) to the *trans*-isomer *XXIb*, in analogy to *cis*- and *trans*-decalin[13]. The D/E fusion affects markedly the C-13 signal: *cis*-fusion leads to a γ-gauche arrangement of the C-13 carbon atom relative to the C-20 and C-22 atoms and one can therefore expect an upfield shift of the C-13 signal compared with that of D/E – *trans*-fused derivatives in which there is no such arrangement of carbon atoms. In accord with this, the C-13 signal in the spectra of D/E *trans*-derivatives *XXIV* and *XXV* appears at δ 43–44 and for dienes *I–IV* at $\delta \approx 42$, whereas for compounds *V–IX*, *XIII*, *XXIa* and *XXIII* with *cis*-annelated rings it is located in the region δ 34–38. The *trans*-diketone *XXIb* represents an exception: in this compound the low value for C-13 (δ 37·1) is due to the upfield effect of the carbonyl group on C-19.

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. Optical rotation was measured in chloroform on an automatic polarimeter ETL-NPL (Bendix–Ericsson), accuracy ±2°. IR spectra were measured in chloroform solutions (unless stated otherwise) on a UR-10, UR-20 or a Unicam SP-700 instrument; wavenumbers in cm^{-1}. UV spectra were taken in ethanol (unless stated otherwise) on a Unicam SP-700 spectrophotometer. ^1H NMR spectra were obtained with CW NMR spectrometers Varian A-60 (60 MHz) and Varian HA-100 (100 MHz) or with FT NMR instruments Varian XL-200 (200 MHz), Bruker (360 MHz) or Varian UNITY 500 (500 MHz) in deuterochloroform with tetramethylsilane as internal standard. ^1H NMR spectra of compounds *XIII*, *XX* and *XXIV* were also measured in hexadeuterobenzene, the chemical shifts were related to tetramethylsilane using the relation $\delta(C_6D_5H) = 7{\cdot}37$. Proton-decoupled ^{13}C NMR spectra were taken on a Varian XL-200 (50·31 MHz) instrument in deuterochloroform using the APT pulse sequence[14]. Optical rotatory dispersion was measured on a Jasco-ORD/UV-5 instrument in dioxane and CD spectra were taken on a Roussel–Jouan 185 instrument in dioxane. Mass spectra were obtained on a Varian MAT 311 spectrometer (70 eV, ionizing current 1 mA, ion source temperature 200°C, direct inlet system temperature 90–150°C). The ion composition (when given) was veliffed by high resolution with an error less than 5 ppm. Chromatography was performed on neutral alumina (activity II according to Brockmann) or

on silica gel (according to Pitra). Analytical samples were dried under diminished pressure at 100°C over phosphorus pentoxide for 10 h. The "usual work-up procedure" consists in dilution of the reaction mixture with water, extraction of the product with ether, repeated washing of the ethereal extract successively with water, dilute hydrochloric acid (1 : 4), water and 5% solution of sodium carbonate. All solutions were dried over anhydrous sodium sulfate. The identity of the samples was proven by mixture melting point, optical rotation, TLC and IR spectra.

19-Isopropylidene-28,29,30-trinor-18α-olean-17(22)-ene (ref.[1], *I*)

Mass spectrum, *m/z* (%): 408 (M^+, 31, $C_{30}H_{48}$), 393 (3), 365 (3), 231 (80, $C_{17}H_{27}$), 191 (78, $C_{14}H_{23}$), 175 (27), 148 (30), 135 (100, $C_{10}H_{15}$).

3β-Acetoxy-19-isopropylidene-28,29,30-trinor-18α-olean-17(22)-ene (ref.[1], *III*)

Mass spectrum, *m/z* (%): 466 (M^+, 33, $C_{32}H_{50}O_2$), 451 (3), 406 (8), 391 (4), 363 (5), 289 (44, $C_{19}H_{29}O_2$), 229 (40, $C_{17}H_{25}$), 189 (55), 175 (62), 148 (34), 135 (100 $C_{10}H_{15}$).

19-Isopropylidene-28,29,30-trinor-17α,18α-oleanan-3β-ol (ref.[1], *V*)

Mass spectrum, *m/z* (%): 426 (M^+, 12), 411 (5), 408 (5), 207 (95), 189 (95), 175 (30), 163 (40), 149 (81), 136 (65), 135 (100, $C_{10}H_{15}$).

3β-Acetoxy-19-isopropylidene-28,29,30-trinor-17α,18α-oleanane (ref.[1], *VI*)

Mass spectrum, *m/z* (%): 468 (M^+, 55), 453 (3), 425 (5), 408 (13), 393 (5), 365 (9), 289 (15, $C_{19}H_{29}O_2$), 249 (10), 229 (25, $C_{17}H_{25}$), 189 (80), 149 (24), 136 (60), 135 (100).

19-Isopropylidene-28,29,30-trinor-17α,18α-oleanan-22α-ol (*VIII*)

Diborane (generated from 0·77 g of sodium borohydride and boron trifluoride etherate (5·0 ml) was introduced during 90 min into an ice-cooled solution of diene[1] *I* (5·5 g) in tetrahydrofuran (350 ml). After standing overnight at room temperature, the reaction mixture was mixed with a solution of sodium hydroxide (5·0 g) in water (50 ml), and 30% hydrogen peroxide (25 ml) was added in portions. The mixture was shaken for 3 h, diluted with water, extracted with ether and the ethereal layer was washed with water and dried. The residue was chromatographed on alumina (150 g) in cyclohexane–ether (4 : 1; 500 ml) to yield the hydroxy derivative *VIII* (5·14 g, 90%), m.p. 250·5–252°C (chloroform–methanol); $[\alpha]_D$ −36° (*c* 1·47). IR spectrum: 3 600, 1 028 (OH); (tetrachloromethane, *c* 2·74 . 10^{-3} mol l^{-1}): 3 624, $\varepsilon' = 36$, $\Delta\nu_{1/2} = 22\ cm^{-1}$, $B =$ = 1 200; 3 600, $\varepsilon' = 20$, $\Delta\nu_{1/2} = 20\ cm^{-1}$, $B = 640$ (OH). ^1H and ^{13}C NMR spectra — see Tables I and II. Mass spectrum, *m/z* (%): 426 (M^+, 45), 411 (5), 408 (16), 393 (5), 231 (85, $C_{17}H_{27}$), 191 (100, $C_{14}H_{23}$), 137 (9, $C_9H_{13}O : C_{10}H_{17} = 5 : 1$), 135 (60, $C_{10}H_{15}$). For $C_{30}H_{50}O$ (426·7) calculated: 84·44% C, 11·81% H; found: 84·50% C, 11·55% H.

22α-Acetoxy-19-isopropylidene-28,29,30-trinor-17α,18α-oleanane (*IX*)

Acetic anhydride (9 ml) was added to a solution of alcohol *VIII* (1·6 g) in pyridine (18 ml), the mixture was heated on a water bath and then set aside at room temperature overnight. The separated crystals were collected and recrystallized from benzene–ethanol; yield 1·0 g (57%) of acetate *IX*, m.p. 212–214°C; $[\alpha]_D$ −13·5° (*c* 0·86). IR spectrum: 1 730, 1 258 (OAc). For ^1H and ^{13}C NMR spectra see Tables I and II. Mass spectrum, *m/z* (%): 468 (M^+, 15), 453 (4),

408 (95), 393 (10), 365 (4), 231 (100, $C_{17}H_{27}$), 191 (95), 135 (98, $C_{10}H_{15}$). For $C_{32}H_{52}O_2$ (468·7) calculated: 81·99% C, 11·18% H; found: 82·08% C, 11·09% H.

19-Isopropylidene-28,29,30-trinor-17α,18α-oleanane-3β,22α-diol (*X*) and 3β,22α-Diacetoxy-19--isopropylidene-28,29,30-trinor-17α,18α-oleanane (*XII*)

Diol *X* was prepared from diene *II* (1·71 g) in the same manner as described for the alcohol *VIII*. The isolated product (1·3 g) was chromatographed on alumina (200 g) in benzene. The product was eluted with ether and crystallized from chloroform; yield 0·65 g (37%) of diol *X*, m.p. 262–264°C; $[\alpha]_D$ −33° (*c* 1·0). Acetylation of *X* (200 mg) with acetic anhydride in pyridine afforded the diacetate *XII* (130 mg, 56%) which was crystallized from methanol, m.p. 245 to 247°C; $[\alpha]_D$ +8° (*c* 1·1). IR spectrum: 1 724, 1 250–1 259 (OAc). For ^{1}H NMR spectrum see Table I. For $C_{34}H_{54}O_4$ (526·8) calculated: 77·52% C, 10·33% H; found: 77·60% C, 10·53% H.

3β-Acetoxy-19-isopropylidene-28,29,30-trinor-17α,18α-oleanan-22α-ol (*XI*)

The title compound was prepared from diene *III* (2·28 g) in the same manner as the alcohol *VIII*. The isolated alcohol *XI* (1·71 g, 72%) melted at 242–244·5°C (chloroform–methanol); $[\alpha]_D$ −6·5° (*c* 1·34). IR spectrum: 1 726, 1 256 (OAc); 1 028 (C—O). Mass spectrum: *m/z* (%): 484 (M^+, 18), 466 (20), 440 (5), 424 (15), 406 (13), 289 (32), 229 (33), 189 (100), 137 (55, $C_9H_{13}O$: : $C_{10}H_{17}$ = 5 : 1), 135 (100, $C_{10}H_{15}$). For $C_{32}H_{52}O_3$ (484·8) calculated: 79·28% C, 10·81% H; found: 79·32% C, 10·52% H.

19-Isopropylidene-28,29,30-trinor-17α,18α-oleanan-22-one (*XIII*)

A solution of chromium trioxide (0·9 g) in pyridine (120 ml) was added to a solution of alcohol *VIII* (1·4 g) in pyridine (50 ml) and the reaction mixture was allowed to stand at room temperature for 5 days. After addition of methanol and the usual work-up, the product was chromatographed on alumina (40 g). Benzene (200 ml) eluted the ketone *XIII* (0·74 g, 53%), m.p. 270 to 272°C (chloroform–light petroleum); $[\alpha]_D$ −36° (*c* 0·61). ORD: $[\Theta]_{476}$ −375°, $[\Theta]_{370}$ −640°, $[\Theta]_{345}$ −1 130°, $[\Theta]_{319}$ −2 780°, $[\Theta]_{311}$ −2 180°, $[\Theta]_{297}$ 0°, $[\Theta]_{280}$ 1 950°, $[\Theta]_{270}$ 2 180°, $[\Theta]_{261}$ 2 110°, $[\Theta]_{250}$ 2 630°. CD: Δε −1·15 (305 nm), −1 . 10 (295 nm). IR spectrum: 1 714 (CO); 1 427 (α-CH_2). For ^{1}H and ^{13}C NMR spectra in $CDCl_3$ see Tables I and II. ^{1}H NMR spectrum (60 MHz; C_6D_6): 0·93 s, 3 H (CH_3); 0·94 s, 3 H (CH_3); 1·01 s, 3 H (CH_3); 1·08 s, 6 H (2 × CH_3); 1·70 bs and 1·76 bs, 6 H ($(CH_3)_2C$=); 3·12 m, 1 H (H-17α), *J* = 11·5, 5·0 and 1·5). Mass spectrum, *m/z* (%): 424 (M^+, 25, $C_{30}H_{48}O$), 409 (5), 406 (4), 231 (75), 191 (82), 149 (30), 137 (100, $C_9H_{13}O$: $C_{10}H_{17}$ = 5 : 1). For $C_{30}H_{48}O$ (424·7) calculated: 84·84% C, 11·39% H; found: 84·75% C, 11·20% H. Further elution with benzene (80 ml) afforded the starting alcohol *VIII* (0·39 g).

Equilibration: A mixture of ketone *XIII* (250 mg), benzene (60 ml) and 0·4M methanolic potassium hydroxide (60 ml) was set aside at room temperature for 48 h, diluted with water and extracted with ether. The ethereal solution was washed with water, dried and the solvent evaporated. The residue had $[\alpha]_D$ −36° (*c* 1·76).

3β-Acetoxy-19-isopropylidene-28,29,30-trinor-17α,18α-oleanan-22-one (*XV*)

A solution of chromium trioxide (0·55 g) in pyridine (30 ml) was added to a solution of monoacetate *XI* (0·82 g) in pyridine (25 ml) and the mixture was allowed to stand at room temperature for 2 days. The material, obtained by the usual work-up procedure, was dissolved in benzene

and chromatographed on alumina (65 g) in benzene. The eluted product was twice crystallized from chloroform–methanol; yield of *XV* 0·38 g (46%), m.p. 239–240°C; $[\alpha]_D$ −16° (*c* 1·93). UV spectrum: λ_{max} 289 nm (log ε) 1·57. IR spectrum: 1 710 (CO); 1 422 (α-CH_2); 1 724, 1 250 (OAc). For ^{1}H NMR spectrum see Table I. For $C_{32}H_{50}O_3$ (482·7) calculated: 79·62% C, 10·44% H; found: 79·80% C, 10·51% H.

3β-Hydroxy-19-isopropylidene-28,29,30-trinor-17α,18α-oleanan-22-one (*XIV*)

A mixture of acetate *XV* (180 mg), ethanol (20 ml) and 8% ethanolic potassium hydroxide (30 ml) was refluxed for 4 h. After cooling, the separated crystals (100 mg) were washed with ethanol and crystallized from chloroform–methanol to give 70 g (43%) of hydroxy ketone *XIV*, m.p. 255–257°C. IR spectrum: 1 704 (CO); 1 423 (α-CH_2); 3 610, 1 027 (OH). For $C_{30}H_{48}O_2$ (440·7) calculated: 81·76% C, 10·98% H; found: 81·88% C, 11·03% H.

19-Isopropylidene-28,29,30-trinor-17α,18α-oleanane-3,22-dione (*XVI*)

A solution of chromium trioxide (80 mg) in pyridine (10 ml) was added to a solution of hydroxy ketone *XIV* (200 mg) in pyridine (10 ml). After standing at room temperature for 4 days, the mixture was worked up as usual. The product (160 mg) on two crystallizations from chloroform–methanol afforded 110 mg (55%) of diketone *XVI*, m.p. 244–246°C; $[\alpha]_D$ −14° (*c* 0·76). IR spectrum: 1 709, 1 700 (CO); 1 427 (α-CH_2). For ^{1}H NMR spectrum see Table I. Mass spectrum, *m/z* (%): 438 (M^+, 17), 423 (5), 420 (5), 395 (5), 245 (38), 205 (15), 149 (17), 137 (100).

22-Acetoxy-19-isopropylidene-28,29,30-trinor-18α-olean-17(22)-ene (*XVII*)

A solution of ketone *XIII* (130 mg) and *p*-toluenesulfonic acid monohydrate (40 mg) in acetic anhydride (10 ml) was refluxed for 4 h. After evaporation of the acetic anhydride in vacuo, the residue was dissolved in ether, the ethereal solution was washed with 5% solution of sodium hydrogen carbonate, water and dried by filtration through a layer of alumina. Yield 85 mg (57%) of *XVII*, m.p. 203–205°C (ether–hexane); $[\alpha]_D$ −93° (*c* 0·71). IR spectrum: 1 748, 1 248 (OAc); 1 711 (C=C). For ^{1}H NMR spectrum see Table I.

17-Bromo-19-isopropylidene-28,29,30-trinor-17α,18α-oleanan-22-one (*XVIII*)

A solution of bromine (18 mg) in acetic acid (5 ml) was slowly added dropwise to a stirred solution of enol acetate *XVII* (50 mg) in a mixture of acetic acid (50 ml) and pyridine (2 ml). After standing in the dark for 1 h, the reaction mixture was diluted with ether, washed with water and 5% sodium hydrogen carbonate, the solution was dried and the solvent evaporated to dryness. The crude product was chromatographed on silica gel (8 g). Light petroleum with 1% ether (50 ml) eluted 22 mg (44%) of bromoketone *XVIII*, m.p. 197–201°C (decomp., ether–hexane); $[\alpha_D]$ −132° (*c* 1·11). ORD: $[\Theta]_{400}$ −2 831°, $[\Theta]_{380}$ −4 023°, $[\Theta]_{360}$ −7 152°, $[\Theta]_{350}$ −10 730°, $[\Theta]_{345}$ −12 370°, $[\Theta]_{339}$ −13 260°, $[\Theta]_{335}$ −12 960°, $[\Theta]_{315}$ 0°, $[\Theta]_{300}$ 9 983°, $[\Theta]_{293}$ 12 810°, $[\Theta]_{285}$ 12 370°, $[\Theta]_{272}$ 9 983°, $[\Theta]_{260}$ 12 810°. CD: Δε −2·02 (293 nm), −2·02 (298 nm). IR spectrum: 1 710 (CO); 1 422 (α-CH_2). Further elution with the same solvent mixture (40 ml) afforded 20 mg of the starting enol acetate *XVII*.

22α-Acetoxy-28,29,30-trinor-17α,18α-oleanan-19-one (*XX*)

Ozone was introduced at −78°C in to a solution of acetate *IX* (1·96 g) in ethyl acetate (300 ml) until the blue colour of the solution became permanent. Most of the solvent was evaporated at

room temperature in vacuo and the residue was mixed with 80% acetic acid (40 ml) and zinc powder. After standing at room temperature for 3 days, the remaining zinc was filtered off. The filtrate was diluted with ether, repeatedly washed with water and 5% solution of sodium carbonate, dried and the solvent was evaporated. The residue (1·24 g) was chromatographed on silica gel (100 g) in light petroleum containing 10% ether (480 ml) to give 535 mg (29%) of ketone *XX*, m.p. 221·5–222°C (benzene–ethanol); $[\alpha]_D$ −34° (*c* 1·33). ORD: $[\Theta]_{500}$ 50°, $[\Theta]_{441}$ 0°, $[\Theta]_{357}$ −1 020°, $[\Theta]_{321}$ −5 220°, $[\Theta]_{313}$ −4 120°, $[\Theta]_{301}$ 0°, $[\Theta]_{286}$ 5 180°, $[\Theta]_{275}$ 6 050°, $[\Theta]_{250}$ 4 080°, $[\Theta]_{230}$ 3 200°, $[\Theta]_{217}$ 4 680°. UV spectrum: λ_{max} 295 nm (log ε 2·10). IR spectrum: 1 711 (CO); 1 437 (α-CH_2); 1 726, 1 253 (OAc). ^{1}H NMR spectrum in $CDCl_3$ — see Table I. ^{1}H NMR spectrum (60 MHz; C_6D_6): 0·89 s, 3 H (CH_3); 0·92 bs, 3 H (CH_3); 0·945 s, 3 H (CH_3); 0·995 s, 3 H (CH_3); 1·12 s, 3 H (CH_3); 1·79 s, 3 H (OAc). Mass spectrum, *m/z* (%): 442 (M^+, 9), 427 (4), 382 (43), 191 (100), 177 (10). For $C_{29}H_{46}O_3$ (442·7) calculated: 78·68% C, 10·47% H; found: 78·49% C, 10·30% H.

22α-Hydroxy-28,29,30-trinor-17α,18α-oleanan-19-one (*XIX*)

Ethanolic solution of potassium hydroxide (97 mg in 6 ml, i.e. 2·94 molar excess) was added to a solution of acetate *XX* (325 mg) in benzene (3 ml). After standing at room temperature for 28 h, the separated hydroxy ketone *XIX* was collected, dissolved in chloroform (10 ml) and the solution was filtered through short column of alumina. The solvent was evaporated and the residue crystallized from ethyl acetate; yield 230 mg (71%) of *XIX*, m.p. 296–297°C; $[\alpha]_D$ −54° (*c* 0·62). IR spectrum: 3 600, 1 060 (OH); 1 705 (CO); 1 436 (α-CH_2). For ^{1}H NMR spectrum see Table I. Mass spectrum, *m/z* (%): 400 (M^+, 14), 385 (4), 382 (4), 191 (100), 177 (15). For $C_{27}H_{44}O_2$ (400·6) calculated: 80·94% C, 11·07% H; found: 81·11% C, 10·94% H.

28,29,30-Trinor-17α,18α-oleanane-19,22-dione (*XXIa*)
and 28,29,30-Trinor-17β,18α-oleanane-19,22-dione (*XXIb*)

Chromium trioxide (60 mg) was added to a stirred and cooled solution of alcohol *XIX* (100 mg) in pyridine (6 ml). After standing at room temperature for 36 h the reaction mixture was worked up as usual. Crystallization from ethyl acetate–ethanol afforded 70 mg (70%) of a mixture of diketones *XXIa* and *XXIb*, m.p. 234–235°C; $[\alpha]_D$ −12° (*c* 0·57). ORD: $[\Theta]_{435}$ −210°, $[\Theta]_{370}$ −620°, $[\Theta]_{345}$ −1 360°, $[\Theta]_{317}$ −4 650°, $[\Theta]_{299}$ 0°, $[\Theta]_{279}$ 6 400°, $[\Theta]_{270}$ 7 370°, $[\Theta]_{244}$ 6 010°, $[\Theta]_{227}$ 7 370°. UV spectrum: λ_{max} 281 nm (log ε 2·12), 292 nm (log ε 2·15). IR spectrum: 1 716 (CO); 1 446 (α-CH_2). For ^{1}H and ^{13}C NMR spectrum see Tables I and II. Mass spectrum: 398 (M^+, 13), 383 (M − 15, 6), 191 (100). For $C_{27}H_{42}O_2$ (398·6) calculated: 81·35% C, 10·62% H; found: 81·19% C, 10·74% H. ORD (dioxane, 0·1M HCl, room temperaure): *a* −120 (317/278 nm); after 24 h: *a* −160 (317/278 nm).

28,29,30-Trinor-18α-oleanan-22-one (*XXIV*)

A solution of ketone *XX* (0·5 g) in benzene (10 ml) was mixed with 85% hydrazine hydrate (5 ml), and ethanol was added until the mixture became homogeneous. The mixture was refluxed for 3 h and then concentrated to a hlaf. The concentrate was heated with hydrazine hydrate (2 ml), diethylene glycol (30 ml) and potassium hydroxide (1 g) to 220°C for 2·5 h. The usual work-up procedure afforded 0·3 g (67%) of amorphous alcohol *XXIII*. IR spectrum: 3 620, 3 460, 1 035 (OH). For ^{1}H and ^{13}C NMR spectrum see Tables I and II. Alcohol *XXIII* (0·3 g) was dissolved in acetone and Jones reagent was added till the first positive reaction with iodide-starch paper was observed. After addition of methanol, the mixture was concentrated in vacuo at room tempera-

ture, diluted with water and extracted with ether. The ethereal extract was washed with water, 5% solution of sodium carbonate, again with water, dried and the solvent was evaporated. The residue was chromatographed on alumina (25 g). Elution with benzene (90 ml) and subsequent crystallization from benzene–ethanol afforded 160 mg (53%) of ketone *XXIV*, m.p. 239·5–240·5°C; $[\alpha]_D$ +29° (*c* 0·64). ORD: $[\Theta]_{385}$ 0°, $[\Theta]_{303}$ −2 712°, $[\Theta]_{265}$ 5 423°, $[\Theta]_{244}$ 4 962°, $[\Theta]_{213}$ 7 846. IR spectrum: 1 704 (CO); 1 430 (α-CH_2). For ^{1}H and ^{13}C NMR spectrum see Tables I and II. ^{1}H NMR spectrum (60 MHz; C_6D_6): 0·89 s, 3 H (CH_3); 0·98 s, 6 H (2 × × CH_3); 1·02 s, 3 H (CH_3); 1·06 s, 3 H (CH_3). Mass spectrum, *m/z* (%): 384 (M^+, 32), 369 (11), 366 (2), 351 (3), 328 (4), 246 (6), 231 (9), 191 (100).

Equilibration: Ketone *XXIV* (80 mg) was equilibrated under the same conditions as ketone *XIII*. The evaporation residue had $[\alpha]_D$ +26° (*c* 0·69).

28,29,30-Trinor-18α-oleanan-22α-ol (*XXV*) and 28,29,30-Trinor-18α-oleanan-22β-ol (*XXVI*)

A solution of ketone *XXIV* (80 mg) in benzene (5 ml) was mixed with methanol (10 ml) and sodium bnrohydride (100 mg). After standing at room temperature overnight, the reaction mixture was worked up as usual and the product was chromatographed on alumina (15 g). Elution with light petroleum–benzene (1 : 1, 60 ml) afforded 30 mg (38%) of alcohol *XXV*, m.p. 239–240°C (chloroform–methanol); $[\alpha]_D$ +43° (*c* 0·49). IR spectrum (tetrachloromethane, *c* 2·87 . 10^{-3} mol l^{-1}): 3 629, $\varepsilon' = 51$, $\Delta\nu_{1/2} = 17$ cm^{-1}, $B = 1\,350$; 3 618, $\varepsilon' = 9$, $\Delta\nu_{1/2} = 9$ cm^{-1}, $B = 130$ (OH). For ^{1}H and ^{13}C NMR spectrum see Tables I and II. Mass spectrum, *m/z* (%): 386 (M^+, 42), 371 (7), 368 (19), 353 (3), 248 (7), 191 (100), 162 (52). Further elution with the same solvent mixture (50 ml) gave 20 mg (25%) of alcohol *XXVI*, m.p. 234–235°C; $[\alpha]_D$ +11° (*c* 0·66). IR spectrum (tetrachloromethane, *c* 3·18 . 10^{-3} mol l^{-1}): 3 628, $\varepsilon' = 40$, $\Delta\nu_{1/2} = 17$ cm^{-1}, $B = 1\,100$; 3 615, $\varepsilon' = 14$, $\Delta\nu_{1/2} = 12$ cm^{-1}, $B = 270$. For ^{1}H and ^{13}C NMR spectrum see Tables I and II. Mass spectrum, *m/z* (%): 386 (M^+, 32), 371 (11), 368 (3), 353 (3), 330 (2), 248 (10), 191 (100).

19-Isopropylidene-28,29,30-trinor-17α,18α-oleanan-22β-ol (*XXIX*)

Sodium borohydride (200 mg) was added to a solution of ketone *XIII* (174 mg) in a mixture of benzene (20 ml) and methanol (15 ml). After standing at room temperature for 3 days, the reaction mixture was diluted with water, extracted with ether, the ethereal extract was washed with water, dried and the solvent evaporated to dryness. The crude product was subjected to TLC on two plates of silica gel G (200 × 200 × 0·7 mm) in light petroleum–ether (4 : 1). The less polar zone afforded 146 mg (84%) of alcohol *XXIX*, m.p. 254–255°C (chloroform–methanol); $[\alpha]_D$ −56° (*c* 0·54). IR spectrum: 3 613, 1 048, 1 034 (OH). For ^{1}H NMR spectrum see Table I. Mass spectrum, *m/z* (%): 427 (M^+ + 1, 10), 426 (M^+, 12), 411 (5), 408 (10), 393 (5), 231 (75), 191 (100), 137 (55), 135 (40). The more polar zone gave 15·5 mg (9%) of an alcohol identical with *VIII*.

22β-Acetoxy-19-isopropylidene-28,29,30-trinor-17α,18α-oleanane (*XXX*)

A mixture of alcohol *XXIX* (82 mg), acetic anhydride (2 ml) and pyridine (4 ml) was heated to 100°C for 5 h. The usual work-up afforded acetate *XXX* (71 mg, 79%), m.p. 201–204°C (chloroform–methanol); $[\alpha]_D$ −58° (*c* 0·60). IR spectrum: 1 722, 1 251 (OAc). For ^{1}H NMR spectrum see Table I. Mass spectrum, *m/z* (%): 468 (M^+, 10), 453 (2), 408 (30), 393 (8), 365 (5), 231 (54), 191 (100), 135 (62). For $C_{32}H_{52}O_2$ (468·7) calculated: 81·99% C, 11·18% H; found: 82·34% C, 10·99% H.

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