AN UNUSUAL REACTION OF A BRIDGED TRITERPENOID α-DIKETONE WITH ACETIC ANHYDRIDE*

Eva KLINOTOVÁ[a], Václav KŘEČEK[a], Jiří KLINOT[a], Miloš BUDĚŠÍNSKÝ[b],
Jaroslav PODLAHA[a], Jana PODLAHOVÁ[a] and Jiří JEČNÝ[c]

[a] *Department of Chemistry, Charles University, 128 40 Prague 2*
[b] *Institute of Organic Chemistry and Biochemistry,*
Czechoslovak Academy of Sciences, 166 10 Prague 6
[c] *Institute of Macromolecular Chemistry,*
Czechoslovak Academy of Sciences, 162 06 Prague 6

Received February 12, 1991
Accepted February 22, 1991

Dedicated to Professor Alois Vystrčil on the occasion of his 70th birthday.

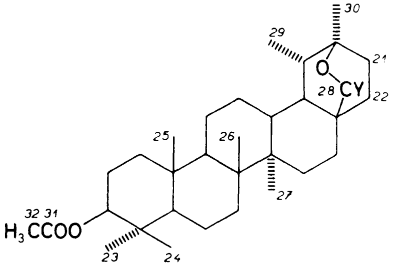
3β-Acetoxy-21,22-dioxo-18α,19β*H*-ursan-28,20β-olide (*IIIa*) reacts with acetic anhydride in pyridine under very mild conditions affording β-lactone *IVa* and γ-lactones *Va* and *VIIa* as condensation products. On reaction with pyridine, lactones *Va* and *VIIa* undergo elimination of acetic acid to give unsaturated lactones *VIIIa* and *IXa*, respectively. Similarly, the condensation of 20β,28-epoxy-21,22-dioxo-18α,19β*H*-ursan-3β-yl acetate (*IIIb*) with acetic anhydride leads to β-lactone *IVb* and γ-lactone *Vb*; the latter on heating with pyridine affords unsaturated lactone *VIIIb* and 21-methylene-22-ketone *Xb*. The structure of the obtained compounds was derived using spectral methods, particularly ^{1}H and ^{13}C NMR spectroscopy; structure of lactone *IVa* was confirmed by X-ray diffraction.

Triterpenoid 21,22-diketones *IIIa* and *IIIb* derived from 3β-acetoxy-18α,19β*H*-ursan-28,20β-olide (*Ia*) and 20β,28-epoxy-18α,19β*H*-ursan-3β-yl acetate (*Ib*), respectively, represent suitable starting material for the preparation of E-seco-acids. In the course of preparation of larger quantities of diketone *IIIa* we have found[1] that it is easily converted into products of dimeric character. Attempting to determine the structure of these products[2] we observed that diketone *IIIa* reacts with acetic anhydride in pyridine under very mild conditions that are usually used in acetylation of hydroxy groups. In this paper we investigate the reaction of 21,22-diketones *IIIa* and *IIIb* with acetic anhydride in pyridine and derive the structure of the arising products (Scheme 1). The studies were performed on two series of derivatives: on compounds with a δ-lactone bridge (28,20β-olides, series *a*), and with an ether bridge on the ring E (20β,28-epoxy compounds, series *b*).

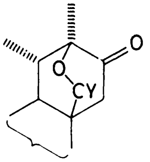
---

* Part XCVI in the series Triterpenes; Part XCV: Collect. Czech. Chem. Commun. *56*, 1732 (1991).

Diketone *IIIa* reacted with acetic anhydride in pyridine at room temperature during 24 h under formation of a mixture which was separated by column chromatography. In 54% yield we obtained a chromatographically unseparable mixture of



Ia, *Ib*



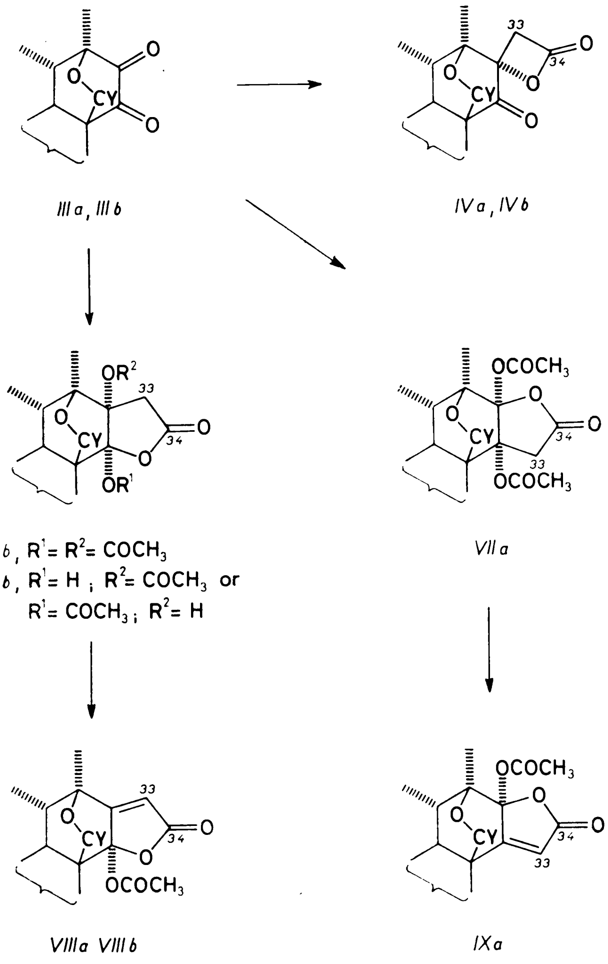
IIa, *IIb*

In formulae *I* and *II*: *a*, Y = O ; *b*, $Y = H_2$

isomers *Va* and *VIIa* containing a γ-lactone ring and two acetoxy groups on the ring E. These isomers were separated by crystallization. According to optical rotation, the ratio *Va* : *VIIa* was about 2 : 1. Further we isolated the β-lactone *IVa* (9%) and the unsaturated lactone *VIIIa* (9%). As shown by thin-layer chromatography (TLC) on silica gel, the mixture also contained a small amount of the unsaturated lactone *IXa*. Lactones *Va* and *VIIa* are evidently precursors of unsaturated lactones *VIIIa* and *IXa*: extension of the reaction time to 7 days or performing the reaction with acetic anhydride in pyridine at reflux increased the amount of the unsaturated lactones *VIIIa* and *IXa* in the reaction mixture (according to TLC) with simultaneous decrease of amount of *Va* and *VIIa*. The elimination of acetic acid also takes place on heating *Va* and *VIIa* in pyridine, the former giving *VIIIa* and the latter *IXa*.

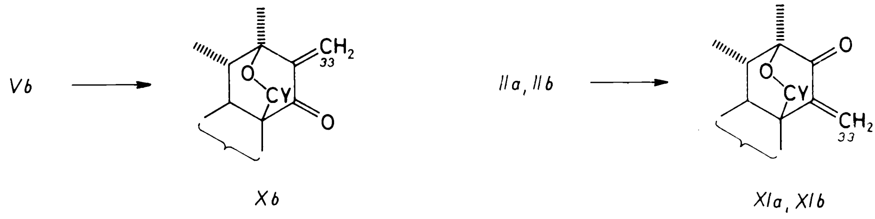
Similarly to the diketone *IIIa*, also the diketone *IIIb* reacted with acetic anhydride in pyridine at room temperature, however, the reaction was substantially slower: even after 7 days we isolated about 8% of the starting *IIIb* from the reaction mixture. As the principal product (59%) we obtained the γ-lactone *Vb* with two acetoxy groups on the ring E. We also isolated the β-lactone *IVb* (6%) and γ-lactone *VIb* (6%) that has only one acetoxy group on the ring E, together with a hydroxy group. No unsaturated lactone *VIIIb* has been found among the products; however, this compound was prepared by heating lactone *Vb* in pyridine. The elimination of acetic acid from *Vb* was again slower than that from lactones of the series *a*; in addition to the unsaturated lactone *VIIIb* the reaction afforded also the methylene ketone *Xb* (Scheme 2).

The position of carbonyl group on C(22) and exocyclic double bond on C(21) in methylene ketone *Xb* was confirmed by synthesis of its isomer, 22-methylene-21-ketone *XIb*, from ketone *IIb* by reaction with formaldehyde and dimethylamine hydrochloride in boiling dioxane. For comparison, we prepared methylene ketone *XIa* from ketone *IIa*. The formation of *Xb* from lactone *Vb* clearly confirms that the methylene (or methine) group of the γ-lactone ring in compounds *Vb* and *VIIIb* is attached to C(21). Thus the condensation of acetic anhydride with diketone *IIIb*



In formulae *III*-*IX*: *a*, $Y = O$; *b*, $Y = H_2$

SCHEME 1

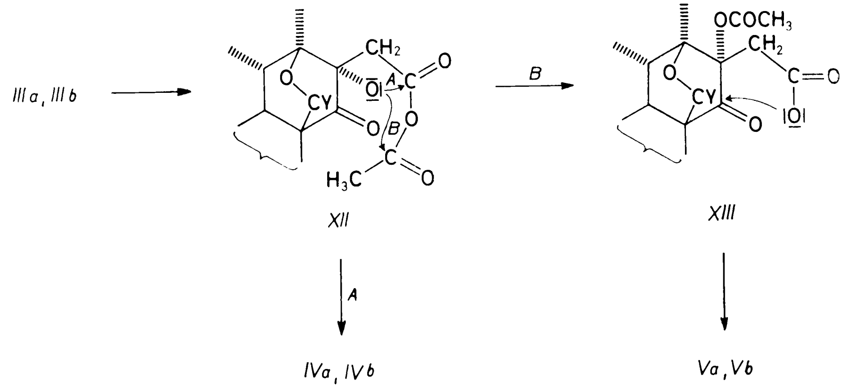


In formulae X and XI: a, Y = O ; b, Y = H$_2$

SCHEME 2

takes place on the carbonyl group in position 21. In the series *a*, the reaction of lactones *Va* and *VIIa* with pyridine did not afford the analogous methylene ketones and therefore we were not able to determine how the lactone ring is annelated in compounds *Va*, *VIIa*–*IXa* as we had done in the series *b*. Structures were assigned to these compounds on the basis of spectral measurements (vide infra). In the case of lactone *VIb* it is not possible to decide whether the hydroxy group is bonded to C(21) or to C(22).

The presence and position of the β-lactone ring in lactone *IVa*, and also the configuration at C(21) was confirmed by X-ray diffraction (vide infra). The structure of the β-lactone *IVb* follows from analogy and from similarity of its NMR and infrared spectra with those of the lactone *IVa*. As regards configuration of the γ-lactones in both series *a* and *b*, we assume that acetic anhydride attacks the diketones *IIIa* and *IIIb* from the sterically less hindered β-side (similarly as in the formation of



In formulae XII and XIII: a, Y = O ; b, Y = H$_2$

SCHEME 3

β-lactone *IVa*) and suggest therefore that all the compounds have β-configuration of the lactone ring in position 21 as well as 22.

The formation of compounds obtained by reaction of diketones *IIIa* and *IIIb* with acetic anhydride may be explained on the basis of Scheme 3. The first step, common for all products, is the attack of one of the keto groups by anion $CH_3COOCOCH_2^{(-)}$ with subsequent intramolecular attack by the alkoxide oxygen atom of either one (path *A*) or the other (path *B*) carbonyl group of the mixed anhydride *XII*. In the former case (*A*), cyclization to β-lactones *IVa* and *IVb* takes place, whereas in the latter (*B*) the acetyl group is transferred to the oxygen atom with subsequent closure of the γ-lactone ring (see formula *XIII*). In accord with the expected reactivity of the keto groups in positions 21 and 22, the condensation with acetic anhydride takes place mainly on the 21- keto group which is adjacent to an electronegative substituent – the oxygen atom of the lactone or ether bridge. It seems that the presence of negative substituent in 2-oxabicyclo[2.2.2]octane system in ring E of diketones *IIIa* and *IIIb* is of principal importance for the reaction since attempts to obtain similar condensation products by reaction of 1,7,7-trimethylbicyclo[2.2.1]heptane-2,3--dione (camphorquinone) with acetic anhydride in pyridine were unsuccessfull even using prolonged reaction time (90 days at room temperature) or higher temperature (reflux for 16 h). The mentioned condensation of diketones *IIIa* and *IIIb* with acetic anhydride represents thus another example of anomalous reactions observed with these bridged systems in the ring E (see ref.[1] and references therein).

Spectral Data

Structure of the prepared compounds was confirmed by ^1H and ^{13}C NMR spectra, infrared spectra and in some cases also by mass spectra. The characteristic ^1H NMR parameters of compounds *IVa,b–XIa,b*, obtained at 200 MHz, are summarized in Table I. For comparison, the table also contains the starting compounds *Ia,b* to *IIIa,b*. Although the data of the starting compounds have already been published[1,3–5], they were obtained from spectra measured at low frequencies (60 to 100 MHz). The assignment of the methyl signals is based on comparison of compounds in the series *a* and *b* and other similar compounds[2] and on the assignment described[3] for lactone *Ia*. For the $C(28)H_2$ protons in the 20β,28-epoxy derivatives (series *b*) the upfield signal (δ 3·1–3·7) was ascribed to H-28(*exo*) on the basis of long-range coupling with H-18α ($J \sim 1·5$ Hz). The assignment of the downfield signal (δ 4·0–4·5) to H-28(*endo*) follows from the long-range coupling with H-22α, observed with compounds *Ib* and *IIb* ($J = 3·1$ and 2·2 Hz, respectively) but absent in *IIIb–XIb* which have no hydrogen atoms on C(22) (see also refs[5,6]).

The chemical shifts of ^{13}C signals are given in Table II. Structural assignment to individual carbon atoms is based on the APT (attached proton test) spectra and for the region of rings A, B, C and partly D on the recently published[7] assignment in taraxasterol acetate (18α,19β*H*-urs-20(30)-en-3β-yl acetate), derived from a two-dimensional ^{13}C—^{13}C connectivity (INADEQUATE) experiment. As regards assignment of carbon atoms in the ring E, in the literature we found ^{13}C NMR spectra of only two compounds derived from 18α,19β*H*-ursan-28,20β-olide: 3β-acetate *Ia* (ref.[4]) and 3β,23-diol (ref.[8]). Unfortunately, chemical shifts of some carbon atoms differ from those found by the authors and our interpretation differs as well. Therefore, the assignment of carbon signals in the ring E and its vicinity is only tentative and follows only from comparison of spectra of compounds in the series *a* and *b* and other analogous compounds[2]. It is uncertain particularly in the case of methine carbon atoms C(13), C(18) and C(19), methylene carbon atoms C(12) and C(15), methyl atoms C(29) and C(30) and in some cases also C(24) and (25) whose chemical shifts differ only slightly. The mentioned signals can be interchanged

TABLE I

Proton NMR parameters, for conditions see Experimental

Parameter	Chemical shifts[a]							
	Ia	*Ib*	*IIa*[b]	*IIb*[c]	*IIIa*	*IIIb*	*IVa*	*IVb*
H-3α[e]	4·47 m	4·48 m	4·47 m	4·49 m	4·47 m	4·48 m	4·47 m	4·48 m
OAc-3β	2·042	2·044	2·046	2·048	2·045	2·047	2·042	2·045
Me-23[f]	0·844	0·840	0·851	0·849	0·853	0·853	0·852	0·851
Me-24[f]	0·834	0·840	0·843	0·849	0·843	0·850	0·840	0·844
Me-25[g]	0·852	0·873	0·871	0·893	0·875	0·901	0·867	0·889
Me-26	0·932	0·983	0·964	1·016	0·978	1·037	0·954	1·024
Me-27	0·903	0·901	0·934	0·928	0·892	0·889	0·908	0·910
H-28en	—	4·13 dd	—	4·34 dd	—	4·51 d	—	4·35 d
H-28ex	—	3·33 dd	—	3·32 dd	—	3·69 dd	—	3·45 dd
J(28en, 28ex)	—	8·7	—	8·8	—	9·7	—	10·2
J(28en, 22α)	—	3·1	—	2·2	—	—	—	—
J(28ex, 18)	—	1·5	—	1·7	—	1·6	—	1·5
Me-29	0·988 d	0·866 d	0·898 d	0·770 d	0·945 d	0·844 d	1·088 d	0·944 d
J(29, 19)	7·0	7·2	7·2	7·1	7·3	7·1	7·3	7·4
Me-30	1·311	1·028	1·378	1·133	1·527	1·269	1·628	1·340
H-33	—	—	—	—	—	—	3·61 d	3·60 d
H-33′	—	—	—	—	—	—	3·40 d	3·32 d
J(33, 33′)	—	—	—	—	—	—	16·8	16·5
OAc-21[h]	—	—	—	—	—	—	—	—
OAc-22[h]	—	—	—	—	—	—	—	—

---

[a] Singlets, unless stated otherwise; [b] 2·19 d and 2·46 d (H-22α and H-22β; *J*(22α, 22β) = 19·3 Hz); [c] 1·98 dd and 2·26 d (H-22α and H-22β; *J*(22α, 22β) = 18·8; *J*(22α, 28en) = 2·2 Hz); [d] 3·64 s (OH); [e] *J*(3α, 2α) + *J*(3α, 2β) ≈ 16 Hz; [f] tentative assignment — signals may be interchanged;

(Table II), other possibilities of signal interchange are indicated in Table II. In spite of this uncertainty in the assignment, the ^{13}C NMR spectra clearly confirm the presence of the correspondingly substituted carbon atoms as given in formulae *I – XI*.

^1H NMR spectra of both β-lactones *IVa* and *IVb* exhibit an AB system of the $C(33)H_2$ protons with $J(33,33') = 16{\cdot}5$ and $16{\cdot}8$ Hz, respectively. Their structural similarity is indicated by very similar chemical shifts of H-33 and H-33' protons (*IVa*: δ 3·61 and 3·40; *IVb*: δ 3·60 and 3·32) and further by shifts of the methyl groups in positions 19α and 20α (Me-29 and Me-30) compared with the shifts of unsubstituted compounds *Ia* and *Ib*: in both the series *a* and *b*, an introduction of a β-lactone and ketone group into the molecule of compound *Ia* or *Ib* results in practically the same changes in shifts of the Me-29 ($\Delta\delta = \delta(IV) - \delta(I) = +0{\cdot}10$

TABLE I

(*Continued*)

and coupling constants[a]

Va	*Vb*	*VIb*[d]	*VIIa*	*VIIIa*	*VIIIb*	*IXa*	*Xb*	*XIa*	*XIb*
4·48 m	4·50 m	4·48 m	4·46 m	4·48 m	4·49 m	4·47 m	4·48 m	4·46 m	4·48 m
2·049	2·054	2·045	2·043	2·048	2·052	2·047	2·044	2·043	2·048
0·863	0·864	0·851	0·834	0·861	0·864	0·858	0·846	0·854	0·851
0·845	0·850	0·843	0·830	0·844	0·851	0·842	0·846	0·845	0·851
0·863	0·894	0·882	0·848	0·861	0·886	0·873	0·886	0·874	0·897
0·946	0·989	0·994[f]	0·899[f]	0·917	1·010	0·959[f]	1·025[f]	0·981	1·038
0·969	0·972	0·947[f]	0·848[f]	0·992	1·003	0·938[f]	0·886[f]	0·922	0·921
—	4·06 d	4·05 d	—	—	3·98 d	—	4·36 d	—	4·38 d
—	3·38 bd	3·28 bd	—	—	3·16 dd	—	3·46 dd	—	3·32 dd
—	9·6	10·3	—	—	10·6	—	9·5	—	8·5
—	—	—	—	—	—	—	—	—	—
—	≦1	≦1	—	—	1·3	—	1·4	—	1·6
1·178 d	1·096 d	1·062 d	1·198 d	1·003 d	0·846 d	1·312 d	0·756 d	0·882 d	0·762 d
7·0	6·7	7·3	7·1	7·1	7·1	6·6	6·9	7·3	7·1
1·497	1·218	1·168	1·541	1·685	1·431	1·585	1·319	1·450	1·209
3·65 d	3·57 d	3·35 d	3·96 d	6·41	6·33	6·13	6·19 d	6·28	6·11 d
3·24 d	3·30 d	2·79 d	3·07 d	—	—	—	5·34 d	5·51	5·29 d
19·6	19·5	18·7	20·0	—	—	—	1·0	≈0	1·0
2·023	1·984	2·156	2·088	—	—	2·111	—	—	—
2·216	2·187	—	2·164	2·112	2·081	—	—	—	—

---

[g] broad singlet and/or doublet with $J \leqq 0{\cdot}5$ Hz; [h] the signals in *Va*, *Vb* and *VIIa* may be interchanged.

TABLE II

Carbon-13 chemical shifts, for conditions see Experimental

Carbon	*Ia*	*Ib*	*IIa*	*IIb*	*IIIa*	*IIIb*	*IVa*	*Va*	*Vb*	*VIb*	*VIIa*	*VIIIa*	*VIIIb*	*IXa*	*Xb*	*XIb*
1	38·46	38·48	38·43	38·48	38·44	38·45	38·42	38·55	38·55	38·47	38·50	38·47	38·49	38·49	38·49	38·49
2	23·63	23·65	23·58	23·62	23·58	23·59	23·58	23·62	23·62	23·62	23·61	23·62	23·64	23·60	23·64	23·63
3	80·88	80·88	80·74	80·77	80·73	80·69	80·72	80·82	80·79	80·84	80·79	80·79	80·80	80·77	80·82	80·79
4	37·75	37·76	37·73	37·76	37·75	37·75	37·75	37·77	37·77	37·76	37·76	37·77	37·79	37·75	37·78	37·77
5	55·46	55·46	55·41	55·44	55·38	55·39	55·37	55·47	55·49	55·43	55·47	55·44	55·44	55·37	55·44	55·47
6	18·08	18·10	18·03	18·07	18·02	18·02	18·03	18·06	18·05	18·06	18·00	18·06	18·08	18·00	18·09	18·07
7	33·82	33·83	33·79	33·81	33·83	33·83	33·81	34·01	33·96	33·83	33·79	33·77	33·78	34·10	33·87	33·81
8	40·50	40·67	40·53	40·69	40·61	40·71	40·59	40·52	40·59[a]	40·60[a]	40·50	40·50	40·69	40·58	40·73	40·70
9	50·48	50·65	50·35	50·54	50·19	50·36	50·14	50·20	50·34	50·43	50·42	50·38	50·58	49·99	50·50	50·55
10	37·04	37·06	37·02	37·07	37·05	37·05	37·04	37·04	37·04	37·06	37·03	37·07	37·10	37·00	37·08	37·08
11	20·94	21·23	20·84	21·20	20·88	21·19	20·86	20·96	21·32	21·22	20·93	20·76	21·00	20·91	21·26	21·26
12	25·13	25·38	25·38	25·92	25·49	25·98	25·40	26·12	25·78	25·57	25·52	24·93	25·13	26·14	25·67	25·81
13	42·82	39·64	42·70	39·74	43·29	39·84	42·98	43·05	39·05	39·22	42·56	42·67	39·48	41·71	39·38	39·86
14	41·03	41·31	41·05	41·28	40·99	41·04	40·86	40·73	40·80[a]	40·66[a]	40·50	41·27	41·45	40·81	41·13	41·20
15	27·03[a]	26·50	26·87	26·60	25·71	25·65	25·52	26·45	27·14	25·94	26·45	25·84	26·03	26·95	26·06	26·42
16	27·25[a]	29·80	27·00	29·36	19·10	21·09	18·76	19·45	20·11	19·92	21·90	18·86	19·79	22·05	21·01	24·71
17	42·03	34·93	43·99	35·44	62·36	49·10	58·83	51·79	40·54[a]	41·12	53·20	54·67	44·23	50·37	45·58	38·86
18	48·34	47·02	47·34	45·75	44·71	41·61	46·25	39·59	40·75	39·30	39·68	39·02	38·29	46·06	42·51	44·92

19	41·95	42·37	42·15	41·95	41·93	41·57	42·14	43·21	42·46	41·80	40·59	40·63	41·45	43·86	42·37	41·97
20	84·13	72·11	87·94	78·17	87·53	81·37	83·60	84·85^{a}	76·46	74·44	82·61	82·93	75·11	84·08	76·71	78·40
21	32·20	31·66	204·87	209·64	189·23^{a}	197·71^{a}	73·35	82·41^{a}	83·47	87·06	105·79	163·66	166·98^{a}	104·84	144·24	197·30
22	27·52^{a}	27·84	45·45	50·27	188·26^{a}	192·78^{a}	201·44	107·17	108·84	107·57	82·86	104·54	107·85	163·79	201·08	149·41
23	27·90	27·89	27·88	27·88	27·89	27·87	27·91	27·91	27·87	27·89	27·89	27·91	27·90	27·89	27·91	27·90
24	16·45	16·46	16·43	16·46	16·46	16·46	16·47	16·48	16·52	16·46	16·45	16·46	16·46	16·49	16·48	16·46
25	16·33	16·39	16·32	16·43	16·36^{b}	16·46	16·34	16·43	16·48	16·46	16·38	16·29	16·36	16·42^{a}	16·48	16·46
26	15·66	15·73	15·60	15·71	15·61	15·71	15·64	15·70	15·71	15·74	15·54	15·62	15·80	15·71	15·76	15·72
27	14·17	14·20	14·15	14·29	13·98	14·10	14·00	13·73	13·78	13·91	14·14	13·98	14·03	13·81	14·10	14·44
28	177·17	68·96	174·25	68·49	170·99	65·30	168·05	168·67^{b}	64·06	62·84	168·18^{a}	168·53^{a}	62·26	168·57^{b}	64·95	67·66
29	18·70	20·13	18·00	19·37	17·57	19·06	17·23	18·86	21·32^{b}	19·63	17·64	17·99	18·97	19·20	19·62	19·39
30	23·96	24·87	16·32	16·93	16·30^{b}	17·10	17·05	21·80^{c}	21·48^{b}	19·90	17·93	18·94	19·39	16·49^{a}	20·12	17·36
31^{d}	171·01	170·96	170·92	170·93	170·99	170·93	170·95	171·07	171·02	171·00	171·03	171·03	171·03	171·03	170·97	170·98
32^{d}	21·30	21·30	21·25	21·27	21·27	21·28	21·28	21·30	21·32	21·29	21·29	21·29	21·30	21·30	21·30	21·30
33	—	—	—	—	—	—	46·04	35·85	36·02	37·16	34·83	123·77	122·56	119·43	118·51	115·68
34	—	—	—	—	—	—	163·75	167·91^{b}	168·21^{c}	173·35^{b}	168·13^{a}	167·82^{a}	169·01^{a}	167·76^{b}	—	—
OAc:																
C=O^{e}	—	—	—	—	—	—	—	169·38^{b}	169·27^{c}	171·94^{b}	170·15^{a}	169·94^{a}	169·63^{a}	170·34^{b}	—	—
C=O^{e}	—	—	—	—	—	—	—	170·22^{b}	172·46^{c}	—	170·33^{a}	—	—	—	—	—
CH_3^{e}	—	—	—	—	—	—	—	21·30^{c}	21·94^{b}	21·56	21·47	22·16	22·15	22·28	—	—
CH_3^{e}	—	—	—	—	—	—	—	21·35^{c}	21·94^{b}	—	21·66	—	—	—	—	—

[a,b,c] The signals with the same symbols may be interchanged; [d] carbon atoms of 3β-acetoxy group; [e] carbon atoms of acetoxy groups in ring E.

and +0·08 for *IVa* and *IVb*, respectively) and Me-30 signals ($\Delta\delta$ = +0·32 and +0·31 for *IVa* and *IVb*, respectively).

The comparison of ^{1}H NMR spectra allows structural correlation of γ-lactones in the series *b* (*Vb*, *VIIIb*) for which the attachment of C(33) to C(21) is proved in a chemical way (vide supra) with γ-lactones in the series *a* where we obtained two sets of isomers (*Va*, *VIIIa* and *VIIa*, *IXa*) and no information was available in which isomer the C(33) atom is attached to C(21) and in which to C(22). As seen from Table I, the chemical shifts of methylene protons in the lactone ring (H-33, H-33′) of lactone *Va* differ only little from those found for lactone *Vb*; the isomeric lactone *VIIa* exhibits completely different values. Similarly, the singlet of the olefinic proton H-33 in the unsaturated lactone *VIIIa* has a very similar shift to that found in lactone *VIIIb* whereas for isomer *IXa* this value is different. Elimination of acetic acid from lactones *Va* and *Vb* under formation of unsaturated lactones *VIIIa* and *VIIIb* results in an upfield shift of Me-29 ($\Delta\delta = \delta(VIII) - \delta(V) = -0{\cdot}18$ and $-0{\cdot}25$ in the series *a* and *b*, respectively) and a significant downfield shift of Me-30 ($\Delta\delta$ = +0·19 and +0·21). On the other hand, an analogous elimination of acetic acid from the isomeric lactone *VIIa* under formation of unsaturated lactone *IXa* leads to a downfield shift of Me-29 ($\Delta\delta = \delta(IXa) - \delta(VIIa) = +0{\cdot}11$) and a small downfield shift Me-30 ($\Delta\delta$ = +0·04). The chemical shift differences between the unsaturated lactones *VIIIa*, *VIIIb* and unsubstituted derivatives *Ia*, *Ib* are the same in both series *a* and *b* ($\delta(VIII) - \delta(I) \sim 0$ for Me-29 and +0·40 for Me-30). In the case of the isomeric lactone *IXa* ($\delta(IXa) - \delta(Ia) = +0{\cdot}32$ for Me-29 and +0·27 for Me-30) the analogous differences differ substantially from those mentioned above. These facts indicate that γ-lactones *Va*, *VIIIa* have similar structure to that of lactones *Vb*, *VIIIb* and that lactones *VIIa*, *IXa* have a different structure.

Further information on the structure of these lactones was obtained from 500 MHz ^{1}H NMR spectra of unsaturated lactones *VIIIa* and *IXa* in which it was possible to identify signals of protons on C(16): for the lactone *VIIIa*, the doublet of doublets of doublets at δ 2·16 (J = 13·6, 4·4 and 2·4 Hz) can be ascribed to equatorial H-16β and the doublet of triplets at δ 1·85 (J = 13·6, 13·6 and 4·7 Hz) to axial H-16α. In the spectrum of the isomeric lactone *IXa* these signals appear at δ 2·36 (J = 13·8, 4·4 and 2·4 Hz) and 1·86 (J = 13·8, 13·8 and 4·8 Hz). Two-dimensional ROESY spectrum of lactone *IXa* shows a cross-peak between the olefinic proton H-33 and H-16β; the H-16β proton shows cross-peaks with H-16α and further two protons resonating at $\delta \sim$ 2·05 and 1·30 (undoubtedly H-15α and H-15β, respectively). These results confirm that in lactones *IXa* and *VIIa* the C(33) atom is bonded to C(22).

The infrared spectra of most of the mentioned compounds exhibit a complex of several overlapping carbonyl bands. The band at about 1 720 cm^{-1} can be unequivocally assigned to the 3β-acetoxy group carbonyl. Lactones *IVa* and *IVb* exhibit bands at 1 854 and 1 844 cm^{-1}, respectively, which are ascribed to the β-lactone carbonyl, and bands at 1 738 and 1 723 cm^{-1}, respectively, due to the keto group in the ring E. In lactones *V–IX* the γ-lactone carbonyl band appears in the region 1 785 – 1 815 cm^{-1} whereas the δ-lactone carbonyl in compounds of the series *a* is located at 1 755 – 1 775 cm^{-1} and normally is superimposed by the bands of acetoxy groups on the ring E. The spectra of the methylene lactones *X*, *XIa* and *XIb* exhibit a band at about 1 630 cm^{-1} due to double bond stretching vibration, the ketone carbonyl overlaps with the 3β-acetoxy band at about 1 720 cm^{-1}. The C=O frequencies for compounds with greater number of carbonyl groups in the ring E and its vicinity are higher than is usual for simple compounds; this holds particularly for the lactone series *a*. The higher frequencies are probably caused by steric strain as well as dipole–dipole interaction of the C=O groups in cases of cumulation of several such groups close to each other (see also ref.[9]). Infrared spectrum of lactone *VIb* displays a bonded hydroxyl band at 3 544 cm^{-1} and its ^{1}H NMR spectrum shows a O—H proton singlet at δ 3·64.

Crystal Structure of β-Lactone IVa

Final coordinates of non-hydrogen atoms are given in Table III and bond lengths and bond angles in Table IV. Fig. 1 depicts a perspective view of molecule *IVa* with atom numbering. Selected endocyclic torsion angles are shown in Fig. 2*. The structure consists of isolated molecules packed at van der Waals distances. There are no O···O contacts indicative of a dipole–dipole interaction.

The results clearly confirm the presence of β-lactone ring on C(21) and carbonyl group in position 22. As demonstrated by the torsion angles O(3)—C(20)—C(21)—C(33) (−73·4(5)°) and O(3)—C(20)—C(33)—O(5) (−176·5(5)°), the methylene group of the lactone ring (C(33)) is β-oriented, whereas the oxygen atom O(5) is on the α-side. The four-membered ring is practically planar, the deviations of atoms C(21), C(33), C(34) and O(5) from their least squares plane ($\chi^2 = 16{\cdot}0$) being less than 0·02 Å. The geometry of the triterpenoid skeleton is similar to that of other 18α,19β*H*-ursan-28,20β-olide derivatives so far studied by X-ray diffraction (3β-acetoxy derivative *Ia*, ref.[4]; 3β,23-dihydroxy derivative, ref.[8]). The ring E assumes a classical boat conformation with plane of symmetry passing through atoms C(17) and C(20) (asymmetry parameter $\Delta C_s(17) = 1{\cdot}5°$). The boat is slightly flattened in the region of atoms C(19), C(20) and C(21). The lactone bridge in the ring E is not strictly planar and is somewhat twisted in the direction depicted in Fig. 2.

The rings A, B, C and D exist in the chair conformation and in the region of ring B the skeleton is considerably bent, similarly as in the case of other pentacyclic triterpenoids of this type (see e.g. ref.[10]): the angle between the least square planes of atoms C(1), C(2), C(4), C(5) and atoms C(6), C(7), C(9), C(10) is 18°, the angle

---

* Lists of anisotropic displacement parameters, coordinates of hydrogen atoms and structure factors are available from the authors on request.

TABLE III

Atomic coordinates (.10^4) of non-H atoms in lactone *IVa* with estimated standard deviations in parentheses. $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

Atom	x/a	y/b	z/c	$U_{eq}(.10^3)$
O1	1842(6)	−3255(3)	4364(1)	82(2)
O2	1177(5)	−1486(2)	4457(1)	62(1)
O3	3441(5)	941(2)	832(1)	53(1)
O4	4505(5)	2185(2)	1257(1)	61(1)
O5	5468(6)	−1743(2)	560(1)	70(1)
O6	6896(9)	−2096(3)	−45(2)	133(2)
O7	7955(5)	−676(3)	1073(1)	71(1)
C1	262(7)	−1344(4)	3329(1)	56(2)
C2	−144(7)	−1467(4)	3783(1)	63(2)
C3	1558(7)	−1283(4)	4022(1)	54(2)
C4	2377(7)	−137(4)	3978(1)	52(2)
C5	2719(6)	−4(3)	3511(1)	45(1)
C6	3674(7)	1067(3)	3389(1)	51(1)
C7	4558(7)	932(3)	2972(1)	47(1)
C8	3232(6)	601(3)	2632(1)	43(1)
C9	1979(6)	−351(3)	2778(1)	45(1)
C10	1107(6)	−235(3)	3218(1)	46(1)
C11	627(7)	−649(3)	2444(1)	49(1)
C12	1576(7)	−964(3)	2048(1)	50(1)
C13	2987(6)	−136(3)	1901(1)	43(1)
C14	4361(6)	160(3)	2249(1)	45(1)
C15	5671(7)	1048(3)	2087(1)	52(1)
C16	6691(6)	690(4)	1704(1)	51(1)
C17	5446(6)	307(3)	1363(1)	47(1)
C18	3940(6)	−520(3)	1509(1)	45(1)
C19	2606(7)	−750(3)	1154(1)	48(1)
C20	3323(7)	−250(3)	756(1)	51(2)
C21	5270(7)	−584(3)	670(1)	50(1)
C22	6440(7)	−324(3)	1037(1)	48(1)
C23	4204(8)	−118(4)	4201(1)	66(2)
C24	1147(9)	745(4)	4164(1)	67(2)
C25	−436(7)	625(4)	3233(1)	58(2)
C26	2120(7)	1621(3)	2516(1)	51(1)
C27	5497(7)	−853(3)	2361(1)	49(1)
C28	4449(7)	1242(3)	1153(1)	51(2)
C29	2152(8)	−1980(3)	1106(1)	64(2)
C30	2000(7)	−348(4)	405(1)	59(2)
C31	1345(8)	−2534(4)	4583(1)	66(2)
C32	867(9)	−2663(5)	5022(2)	81(2)
C33	6159(8)	−278(4)	261(2)	68(2)
C34	6317(10)	−1482(5)	198(2)	83(2)

TABLE IV

Bond distances and angles in lactone *IVa* with estimated standard deviations in parentheses

Distances, Å		Angles, °	
O1—C31	1·200(6)		
O2—C3	1·475(5)	C3—O2—C31	115·9(3)
O2—C31	1·362(5)		
O3—C20	1·491(4)	C20—O3—C28	115·8(3)
O3—C28	1·340(5)		
O4—C28	1·212(4)		
O5—C21	1·480(4)	C21—O5—C34	91·7(3)
O5—C34	1·379(8)		
O6—C34	1·179(9)		
O7—C22	1·202(6)		
C1—C2	1·526(5)	C2—C1—C10	113·4(3)
C1—C10	1·545(6)		
C2—C3	1·495(7)	C1—C2—C3	109·4(3)
C3—C4	1·542(7)	O2—C3—C2	108·8(3)
		O2—C3—C4	108·7(3)
		C2—C3—C4	114·7(4)
C4—C5	1·560(5)	C3—C4—C5	104·5(3)
C4—C23	1·531(7)	C3—C4—C23	108·2(4)
C4—C24	1·540(7)	C3—C4—C24	112·3(4)
		C5—C4—C23	109·0(3)
		C5—C4—C24	114·2(3)
		C23—C4—C24	108·4(4)
C5—C6	1·548(6)	C4—C5—C6	114·6(3)
C5—C10	1·553(6)	C4—C5—C10	117·7(3)
		C6—C5—C10	110·1(3)
C6—C7	1·523(5)	C5—C6—C7	109·4(3)
C7—C8	1·537(6)	C6—C7—C8	114·1(3)
C8—C9	1·567(6)	C7—C8—C9	110·5(3)
C8—C14	1·601(5)	C7—C8—C14	109·2(3)
C8—C26	1·547(6)	C7—C8—C26	107·4(3)
		C9—C8—C14	106·9(3)
		C9—C8—C26	111·8(3)
		C14—C8—C26	110·9(3)
C9—C10	1·586(5)	C8—C9—C10	116·7(3)
C9—C11	1·525(6)	C8—C9—C11	110·2(3)
		C10—C9—C11	114·3(3)
C10—C25	1·554(7)	C1—C10—C5	108·9(3)
		C1—C10—C9	107·3(3)
		C1—C10—C25	107·6(3)
		C5—C10—C9	105·7(3)
		C5—C10—C25	114·4(3)
		C9—C10—C25	112·7(3)

TABLE IV
(*Continued*)

Distances, Å		Angles, °	
C11—C12	1·525(5)	C9—C11—C12	112·0(3)
C12—C13	1·534(6)	C11—C12—C13	114·1(3)
C13—C14	1·568(5)	C12—C13—C14	111·3(3)
C13—C18	1·539(5)	C12—C13—C18	111·5(3)
		C14—C13—C18	112·7(3)
C14—C15	1·552(6)	C8—C14—C13	108·4(3)
C14—C27	1·547(6)	C8—C14—C15	110·6(3)
		C8—C14—C27	111·6(3)
		C13—C14—C15	108·4(3)
		C13—C14—C27	109·5(3)
		C15—C14—C27	108·3(3)
C15—C16	1·528(5)	C14—C15—C16	112·5(3)
C16—C17	1·521(5)	C15—C16—C17	113·4(3)
C17—C18	1·580(6)	C16—C17—C18	113·6(3)
C17—C22	1·511(5)	C16—C17—C22	112·8(3)
C17—C28	1·530(6)	C16—C17—C28	112·7(3)
		C18—C17—C22	102·8(3)
		C18—C17—C28	106·6(3)
		C22—C17—C28	107·5(3)
C18—C19	1·549(6)	C13—C18—C17	112·0(3)
		C13—C18—C19	113·3(3)
		C17—C18—C19	109·6(3)
C19—C20	1·537(5)	C18—C19—C20	110·3(3)
C19—C29	1·560(5)	C18—C19—C29	112·9(3)
		C20—C19—C29	112·2(3)
C20—C21	1·517(7)	O3—C20—C19	105·8(3)
C20—C30	1·512(6)	O3—C20—C21	104·1(3)
		O3—C20—C30	104·1(3)
		C19—C20—C21	111·9(3)
		C19—C20—C30	113·2(3)
		C21—C20—C30	116·4(3)
C21—C22	1·514(6)	O5—C21—C20	113·6(3)
C21—C33	1·539(7)	O5—C21—C22	110·0(3)
		O5—C21—C33	89·0(3)
		C20—C21—C22	109·4(3)
		C20—C21—C33	119·8(3)
		C22—C21—C33	113·5(4)
		O7—C22—C17	124·4(3)
		O7—C22—C21	121·9(3)
		C17—C22—C21	113·3(3)
		O3—C28—O4	120·4(3)
		O3—C28—C17	114·2(3)
		O4—C28—C17	125·4(3)

TABLE IV
(*Continued*)

Distances, Å		Angles, °	
C31—C32	1·490(7)	O1—C31—O2	123·3(3)
		O1—C31—C32	124·8(4)
		O2—C31—C32	111·9(4)
C33—C34	1·503(8)	C21—C33—C34	84·9(4)
		O5—C34—O6	126·6(5)
		O5—C34—C33	94·4(4)
		O6—C34—C33	139·0(5)

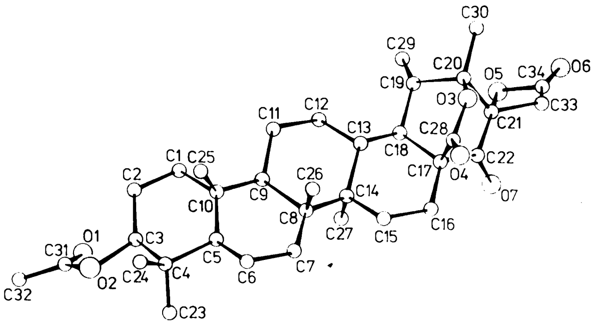


FIG. 1

Perspective view of the molecule *IVa* with atom numbering

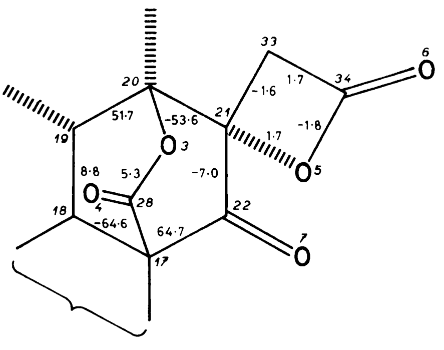


FIG. 2

Selected endocyclic torsion angles in the ring E of lactone *IVa* (estimated standard deviations 0·4—0·5°)

between planes C(1), C(2), C(4), C(5) and C(8), C(11), C(12), C(14) is 32°. The methyl group in position 10β is lent out from the ring B as seen from the angle between bonds C(10)—C(25) and C(8)—C(26) (21°) and between C(10)—C(25) and C(14)—C(27) (160°).

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. Specific rotations were measured in chloroform (c 0·3—0·5) on an automatic polarimeter ETL—NPL (Bendix—Ericsson), accuracy ±2°C. IR spectra were recorded in chloroform on a PE 684 (Perkin-Elmer) spectrometer, wavenumbers are given in cm^{-1}. NMR spectra were measured on a FT-NMR spectrometer Varian XL-200 (^1H at 200 MHz, ^{13}C at 50·31 MHz) at 22°C in deuterochloroform. Tetramethylsilane was used as the internal reference for proton chemical shifts. The values of proton chemical shifts (ppm, δ-scale) and interproton coupling constants (in Hz) were obtained by the first order analysis from the expanded spectra (2 Hz/cm) using the double exponential Lorentz-Gauss function for the resolution enhancement. Carbon-13 chemical shifts were referenced to the signal of solvent and recalculated to tetramethylsilane with the relation $\delta(CDCl_3) = 77{\cdot}0$ ppm. The number of directly bonded hydrogen atoms was determined from the proton decoupled "attached proton test" spectra (APT)[11,12]. For compounds *VIIIa* and *IXa* we also measured the ^1H NMR and 2D-ROESY spectrum (ref.[13]; mixing time 200 ms) on a Bruker AM-500 instrument (at 500 MHz). Mass spectra were measured on an INCOS 50 (Finnigan MAT) spectrometer, ionizing electrons energy 70 eV, ion source temperature 150°C.

The purity of compounds was checked by thin-layer chromatography (TLC), their identity was confirmed by TLC, melting point and infrared spectrum. Thin-layer chromatography was carried out on silica gel G according to Stahl (Merck), column chromatography on silica gel Silpearl (Kavalier, Votice). Analytical samples were dried at 100°C over phosphorus pentoxide under reduced pressure.

The preparation of compounds *Ia* and *Ib* is described in ref.[14], of compounds *IIa* and *IIb* in ref.[9]. Diketones *IIIa* and *IIIb* were prepared by oxidation of the respective ketones *IIa* and *IIb* with selenium dioxide according to ref.[1].

Reaction of 3β-Acetoxy-21,22-dioxo-18α,19β*H*-ursan-28,20β-olide (*IIIa*) with Acetic Anhydride

A solution of diketone *IIIa* (0·20 g) in a mixture of pyridine (2 ml) and acetic anhydride (4 ml) was set aside at room temperature for 24 h. The reaction mixture was decomposed with water and extracted with ether. The ethereal layer was washed with water, dilute hydrochloric acid, water and dried over sodium sulfate. After removal of ether the product mixture (0·2 g) was separated by chromatography on a column of silica gel. Benzene and benzene–ether (10 : 1) mixture eluted successively the following compounds:

β-Lactone *IVa* (0·02 g, 9%), m.p. 287—291°C (decomp.) (chloroform–heptane), $[\alpha]_D$ −4°. IR spectrum: 1 854, 1 772, 1 736, 1 720, 1 256. Mass spectrum, m/z (%): 508 (17; M^+ − 60), 493 (6), 465 (9), 464 (8), 203 (10), 189 (60), 43 (100). For $C_{34}H_{48}O_7$ (568·8) calculated: 71·80% C, 8·51% H; found: 71·52% C, 8·40% H.

Unsaturated lactone *VIIIa* (0·02 g, 9%), m.p. 185—187°C (chloroform–heptane), $[\alpha]_D$ +11°. IR spectrum: 1 806, 1 757, 1 720, 1 256. Mass spectrum, m/z (%): 610 (8; M^+), 595 (9), 566 (15), 550 (3), 507 (10), 203 (15), 189 (86), 43 (100). For $C_{36}H_{50}O_8$ (610·8) calculated: 70·79% C, 8·25% H; found: 70·75% C, 8·41% H.

Chromatographically unseparable mixture of lactones *Va* and *VIIa* (0·14 g, 54%), $[\alpha]_D$ +13°. Repeated crystallization of the mixture from ether afforded lactone *Va* (0·03 g, 12%), m.p. 273–276°C (decomp.), $[\alpha]_D$ +37°. IR spectrum: 1 814, 1 766, 1 718, 1 256. Mass spectrum, *m/z* (%): 610 (15; M^+ – 60), 595 (11), 567 (14), 550 (4), 507 (15), 203 (20), 189 (89), 43 (100). For $C_{38}H_{54}O_{10}$ (670·8) calculated: 68·04% C, 8·11% H; found: 67·83% C, 8·15% H.

The mother liquors from isolation of lactone *Va* on repeated crystallization from chloroform–heptane gave lactone *VIIa* (0·02 g, 8%), m.p. 283–287°C (decomp.), $[\alpha]_D$ –33°. IR spectrum: 1 796, 1 751, 1 724, 1 256. For $C_{38}H_{54}O_{10}$ (670·8) calculated: 68·04% C, 8·11% H; found: 68·11% C, 8·23% H.

Reaction of 20β,28-epoxy-21,22-dioxo-18α,19β*H*-ursan-3β-yl Acetate (*IIIb*) with Acetic Anhydride

A solution of diketone *IIIb* (0·25 g) in a mixture of chloroform (1 ml), pyridine (1 ml) and acetic anhydride (1 ml) was allowed to stand at room temperature for 7 days, the solvents were evaporated under diminished pressure and the residue was separated on a column of silica gel. Elution with benzene and then with benzene–ether (10 : 1) afforded the following compounds:

β-Lactone *IVb* (0·016 g, 6%), m.p. 282–286°C (chloroform–heptane), $[\alpha]_D$ –14°. IR spectrum: 1 843, 1 723, 1 256. Mass spectrum, *m/z* (%): 554 (4; M^+), 510 (11), 494 (2), 450 (9), 203 (14), 189 (62), 43 (100). For $C_{34}H_{50}O_6$ (554·8) calculated: 73·61% C, 9·08% H; found: 73·49% C, 9·15% H.

Starting diketone *IIIb* (0·02 g, 8%).

Lactone *Vb* (0·19 g, 59%), m.p. 290–296°C (decomp.) (chloroform–heptane), $[\alpha]_D$ +75°. IR spectrum: 1 796, 1 752, 1 724, 1 256. For $C_{38}H_{56}O_9$ (656·9) calculated: 69·49% C, 8·59% H; found: 69·23% C, 8·70% H.

Lactone *VIb* (0·02 g, 7%), m.p. 266–274°C (decomp.) (chloroform–heptane), $[\alpha]_D$ –13°. IR spectrum: 3 544, 1 783, 1 726, 1 256. For $C_{36}H_{54}O_8$ (614·8) calculated: 70·33% C, 8·85% H; found: 70·01% C, 8·74% H.

Reaction of Lactone *Va* in Pyridine

A solution of lactone *Va* (0·03 g) in a mixture of benzene (1 ml) and pyridine (2 ml) was refluxed for 3 h. After cooling, the reaction mixture was poured into dilute hydrochloric acid and extracted with ether. The ethereal solution was washed with water and dried by passing through a layer of alumina. Ether was evaporated and the residue (0·025 g) was purified by preparative TLC in benzene–ether (4 : 1). The obtained unsaturated lactone *VIIIa* (0·018 g, 66%) was identical with the sample described above.

Reaction of Lactone *VIIa* in Pyridine

Lactone *VIIa* (10 mg) was subjected to the same procedure as described in the preceding experiment and afforded unsaturated lactone *IXa* (6 mg, 66%), m.p. 255–257°C (chloroform-cyclohexane), $[\alpha]_D$ –88°. IR spectrum: 1 803, 1 763, 1 720, 1 634, 1 255. For $C_{36}H_{50}O_8$ (610·8) calculated: 70·79% C, 8·25% H; found: 70·65% C, 8·28% H.

Reaction of Lactone *Vb* in Pyridine

A solution of lactone *Vb* (0·1 g) in a mixture of benzene (1 ml) and pyridine (4 ml) was refluxed for 37 h. The reaction mixture was diluted with water and extracted with ether. The ethereal solution was washed with dilute hydrochloric acid and water and dried over sodium sulfate.

After evaporation of ether, the residue (0·1 g) was separated by preparative TLC in benzene–ether (7 : 2), affording 20β,28-epoxy-21-methylene-22-oxo-18α,19β*H*-ursan-3β-yl acetate (*Xb*; 0·016 g, 20%), m.p. 309—314°C (decomp.) (chloroform–cyclohexane), $[\alpha]_D$ +17°. IR spectrum: 1 716, 1 631, 1 256. Mass spectrum, *m*/*z* (%): 510 (13; M^+), 450 (11), 407 (6), 203 (9), 189 (23), 43 (100). For $C_{33}H_{50}O_4$ (510·8) calculated: 77·60% C, 9·87% H; found: 77·23% C, 9·76% H. The chromatography gave also lactone *VIIIb* (0·03 g, 31%), m.p. 275—278°C (chloroform–heptane), $[\alpha]_D$ −11°. IR spectrum: 1 791, 1 770, 1 749, 1 720, 1 256. For $C_{36}H_{52}O_7$ (596·8) calculated: 72·45% C, 8·78% H; found: 72·38% C, 8·86% H.

20β,28-Epoxy-22-methylene-21-oxo-18α,19β*H*-ursan-3β-yl Acetate (*XIb*)

A mixture of ketone *IIb* (0·29 g), paraformaldehyde (0·15 g) and dimethylamine hydrochloride (0·20 g) in dioxane (15 ml) was refluxed for 50 h. During this time another portion of paraformaldehyde (0·40 g) and dimethylamine hydrochloride (0·20 g) was added. The reaction mixture was poured into water, extracted with chloroform and the chloroform solution was washed with water and dried over sodium sulfate. The solvent was evaporated and the residue (0·16 g) was chromatographed on a column of silica gel. Elution with benzene–ether (10 : 1) gave the unreacted starting ketone *IIb* (0·12 g, 40%) and then methylene ketone *XIb* (28 mg, 9%), m.p. 315—321°C (decomp.) (ether), $[\alpha]_D$ +76. IR spectrum: 1 718, 1 625, 1 256. Mass spectrum, *m*/*z* (%): 510 (23; M^+), 482 (4), 450 (4), 203 (7), 189 (13), 43 (100). For $C_{33}H_{50}O_4$ (510·8) calculated: 77·60% C, 9·87% H; found: 77·72% C, 9·74% H.

3β-Acetoxy-22-methylen-21-oxo-18α,19β*H*-ursan-28,20β-olide (*XIa*)

Ketone *IIa* (0·22 g) was converted into methylene ketone *XIa* (0·06 g, 26%) as described for the preparation of *XIb*; m.p. 346—347°C (chloroform–heptane), $[\alpha]_D$ +62°. IR spectrum: 1 754, 1 724, 1 629, 1 254. Mass spectrum, *m*/*z* (%): 524 (1; M^+), 480 (1), 464 (20), 421 (32), 203 (12), 189 (45), 43 (100). For $C_{33}H_{48}O_5$ (524·7) calculated: 75·53% C, 9·22% H; found: 75·41% C, 9·36% H.

Crystal Structure Determination

Single crystals of lactone *IVa* were obtained by slow diffusion of pentane vapour through a narrow-bore capillary into a 5% solution in chloroform. Crystal data: $C_{34}H_{48}O_7$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}360(4)$, $b = 12{\cdot}324(6)$, $c = 32{\cdot}79(3)$ Å, $V = 2\,974(3)$ Å^3, $Z = 4$, $\varrho_c = 1{\cdot}272$, $\varrho_m = 1{\cdot}263(5)$ g cm^{-3} (flotation in aqueous $ZnBr_2$), $F(000) = 1\,232$. An 0·4 × 03 × 0·1 mm^3 crystal was measured at room temperature on a Syntex $P2_1$ diffractometer with CuK_α radiation, $\lambda = 1{\cdot}5418$ Å. Lattice parameters were obtained from 15 reflections in the $4 < \Theta < 12{\cdot}5°$ range. Using a $\omega - 2\Theta$ scan mode, intensities were measured in the intervals $\langle 0,8 \rangle$, $\langle 0,13 \rangle$ and $\langle 0,35 \rangle$ for *h*, *k*, *l*, respectively. Three standard reflections monitored after every 47 displayed an overall decrease of 9%; an appropriate correction was applied. From a total of 2 346 reflections, 2 119 fulfilling the criterion $I > 1{\cdot}96\sigma(I)$ were regarded as observed. The structure was solved by direct methods (MULTAN 80)[15] and refined by full-matrix least-squares in two blocks (SHELX76)[16]. Hydrogen atoms were fixed in calculated positions. In the final stages, scale factor, positional and anisotropic displacement parameters of non-H atoms and group (CH_3, CH_2, CH) isotropic displacement parameters of H atoms were refined simultaneously. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 3{\cdot}48/(\sigma^2(F_o) + 0{\cdot}0009F_o^2)$. The refinement converged to $R = 0{\cdot}060$, $wR = 0{\cdot}061$ with extreme values of 0·24; −0·34 e Å^{-3} in the electron density map.

The authors are indebted to Mrs J. Čeřrdlová for elemental analyses and to Dr B. Máca for measurement of mass spectra (both from Department of Organic Chemistry, Charles University, Prague).

REFERENCES

1. Klinotová E., Pavlíková H., Pressová M., Chodounská H., Klinot J., Protiva J., Vystrčil A.: Collect. Czech. Chem. Commun. *52*, 2744 (1987).
2. Klinotová E., Křeček V., Klinot J., Buděšínský M., Hilgard S., Máca B.: Collect. Czech. Chem. Commun., in press.
3. Errington S. G., Jefferies P. R.: Phytochemistry *27*, 543 (1988).
4. Druet D., Comeau L. C., Viani R., Baldy A., Estienne J., Pierrot M.: Can. J. Chem. *65*, 851 (1987).
5. Lehn J. M., Vystrčil A.: Tetrahedron *19*, 1733 (1963).
6. Klinotová E., Beneš J., Vystrčil A.: Collect. Czech. Chem. Commun. *40*, 2861 (1975).
7. Reynolds W. F., Sawyer J. F., Enríquez R. G., Escobar L. I., Chavez M. A., Shoolery J. N.: Can. J. Chem. *63*, 1048 (1985).
8. Atta-ur-Rahman, Ansari A. A., Drexler S. A., Clardy J.: Heterocycles *19*, 217 (1982).
9. Říhová E., Vystrčil A.: Collect. Czech. Chem. Commun. *31*, 3163 (1966).
10. Klinot J., Podlaha J., Podlahová J., Malý K., Petříček V.: Collect. Czech. Chem. Commun. *54*, 725 (1989).
11. Le Cocq C., Lallemand J.-Y.: J. Chem. Soc., Chem. Commun. *1981*, 150.
12. Patt S. L., Shoolery J. N.: J. Magn. Reson. *46*, 535 (1982).
13. Bax A., Davis D. G.: J. Magn. Reson. *63*, 207 (1985).
14. Vystrčil A., Klinot J.: Collect. Czech. Chem. Commun. *24*, 3273 (1959).
15. Main P., Fiske S. J., Hull S. E., Lessinger L., Germain G., Declerq J. P., Woolfson M. M.: MULTAN80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data.* University of York, England and Louvain, Belgium 1980.
16. Sheldrick G.: SHELX76. *Program for Crystal Structure Determination.* University of Cambridge, England 1976.

Translated by M. Tichý.