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Cyclopropanation of Betulin and Its Diacetate with Dihalocarbenes

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Abstract—Reactions of betulin, its diacetate, and 17-acetoxy-28-norlupan-3-one with dichlorocarbene generated from chloroform follow the [1+2]-cycloaddition pattern leading to the corresponding adducts in moderate to quantitative yield. In the reaction with betulin, [1+2]-cycloaddition is accompanied by dichlorocarbene attack on the primary hydroxy group to give the corresponding halogen derivative and formate. The addition of dichlorocarbene to betulin is strictly stereoselective, while the reaction with betulin diacetate affords a mixture of two diastereoisomers at a ratio of 95:5. The reaction of betulin diacetate with dibromocarbene yields dibromocyclopropane derivative which can be converted into the the corresponding diol.

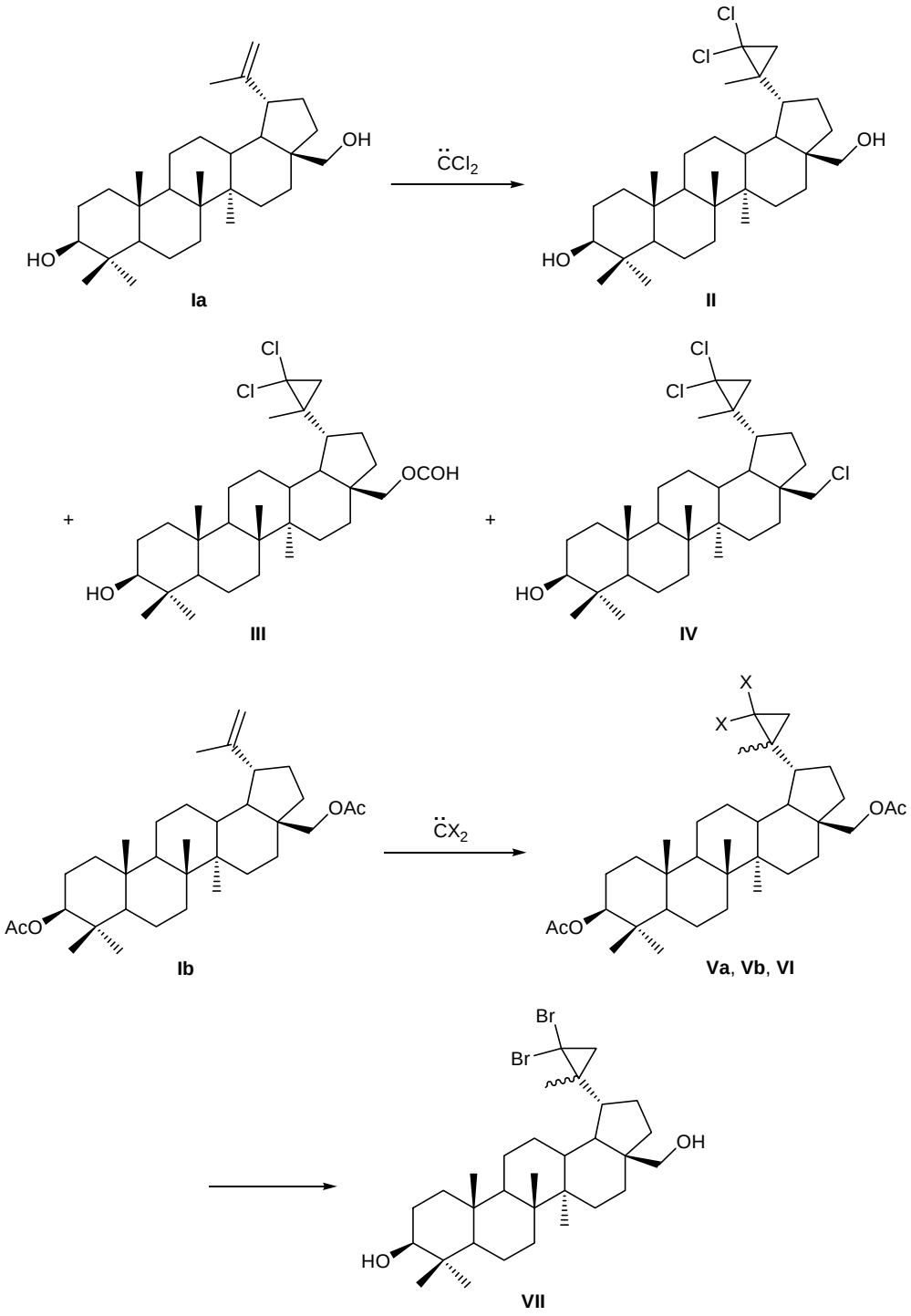
Compounds containing a cyclopropane fragment were found among various naturally occurring biologically active substances, including steroids and terpenoids. The synthetic and biological potentials of these compounds are difficult to overestimate [1, 2]. The presence of an isopropenyl group in molecules of lupane triterpenoids makes it possible to introduce a functionalized cyclopropane moiety into the side chain, thus opening wide prospects in modifying the lupane skeleton at C^{20} and giving rise to new approaches to design of complex molecules on the basis of accessible lupane triterpenoids and to search for new kinds of biological activity in the series of these compounds. Among lupane derivatives containing a cyclopropane fragment, esters derived from betulin (**Ia**) and tetramethylcyclopropanecarboxylic and permetrinic acids have been reported [3].

The double bond in compound **Ia** and its derivatives can be involved in isomerization, oxidation, reduction, and allylic bromination [4–8]. However, despite wide synthetic potential, cyclopropanation of betulin (**Ia**) was not studied. In particular, such experimentally simple and convenient procedure as dihalocyclopropanation of double bond under conditions of phase-transfer catalysis was not applied to betulin [9].

While performing the present study, a publication appeared [10], where a high antituberculous activity was predicted by computer simulation for 20,29-dichloromethanolupane-3β,28-diol and a procedure was proposed for the synthesis of this compound in 35% yield from betulin (**Ia**) in one step under conditions of phase-transfer catalysis. However, no spectral data were given, and the melting point reported therein, 293–294°C, considerably differed from the melting point of a sample prepared by us.

We have found that the reaction of betulin (**Ia**) with dichlorocarbene generated from $CHCl_3$ by the action of 50% aqueous sodium hydroxide in the presence of benzyltriethylammonium chloride at room temperature gives a mixture of dichlorocyclopropanated diol **II**, formate **III**, and chloride **IV** (Scheme 1). The reaction follows the [1+2]-cycloaddition pattern and is accompanied by dichlorocarbene attack on unshared electron pair on the oxygen atom of the primary hydroxy group [11, 12]. Diol **II** was isolated in 55% yield by column chromatography. Formate **III** and chloride **IV** were characterized by similar chromatographic mobilities, so that the former was not identified by TLC, and we isolated a mixture of compounds **III** and **IV** at a ratio of 4:5 (according to the ^{1}H NMR data). The structure of compound **III** followed from the presence in the ^{1}H NMR spectrum of the first eluate fraction of a singlet at δ 8.5 ppm, which is typical of formyl group. In the ^{13}C NMR spectrum we observed a singlet at δ_C 161.47 ppm, which was assigned to the formate moiety, and a triplet at δ_C 62.18 ppm from C^{28}. By subsequent treatment of that fraction with a 5% solution of potassium hydroxide in methanol we obtained

Scheme 1.



Va, **Vb**, X = Cl; **VI**, X = Br.

a mixture of diol **II** and chloride **IV**, and each product was isolated in the pure state by column chromatography. The formation of dichlorocyclopropane ring is confirmed by the absence in the ^{1}H and ^{13}C NMR spectra of **II**–**IV** of downfield signals from protons and carbon atoms at the double bond and the presence in the ^{13}C NMR spectrum of a singlet at δ_C 69.43 ppm, which is typical of a carbon atom attached to two chlorine atoms in cyclopropane ring fragment [13]. The C^{28} signal in the ^{13}C NMR spectra of **II** and **IV**

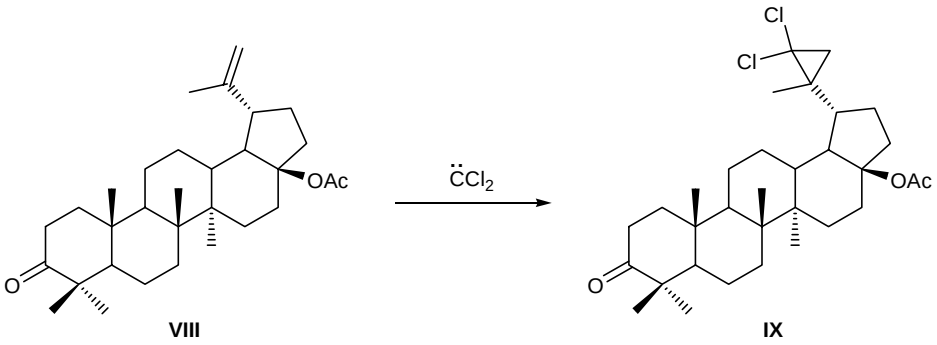
Table 1. ^{13}C and ^{1}H chemical shifts (δ, δ_C, ppm) and coupling constants (J_{HH}) in the NMR spectra of compounds **II**–**IV**

Atom no.	**II**		**III**		**IV**	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
1	38.91	1.08, 1.40	38.80	0.96, 1.70	38.77	0.96, 1.70
2	27.33	1.62	27.42	1.60	27.40	1.60
3	79.01	3.19 d.d (J = 5.2, 11.0)	79.04	3.11 d.d (J = 5.2, 11.0)	79.0	3.2 d.d (J = 5.0, 11.0)
4	38.78		38.94		38.93	
5	55.31	0.70 d (J = 8.6)	55.35	0.70	55.29	0.70 d (J = 8.8)
6	18.24	1.45, 1.58	18.36	1.45	18.35	1.45
7	34.28	1.42	34.24	1.40	34.21	1.20
8	41.00		40.98		40.92	
9	50.21	1.35	50.20	1.35	50.41	1.35
10	37.17		37.18		37.17	
11	20.93	1.17, 1.47	20.90	1.30, 1.50	20.88	1.30, 1.50
12	28.06	1.62, 2.35	27.93	1.65, 2.35	27.85	1.65, 2.35 d.t (J = 4.8, 10.8)
13	36.52	1.60	36.88	1.60	36.64	1.60
14	43.05		43.06		43.09	
15	26.85	1.24, 1.42	26.82	1.40	26.61	1.40
16	29.33	1.25, 1.96 d.q (J = 10.0, 2.0)	29.85	1.25, 1.87	29.83	1.25, 2.12 d (J = 14.2)
17	48.07		46.63		48.28	
18	49.91	1.60	46.91	1.62	46.61	1.58
19	46.97	1.60	49.99	1.63	50.15	1.75
20	34.94		34.87		34.86	
21	26.85	1.04, 1.64	26.81	1.10, 1.60	26.72	1.10, 1.60
22	33.83	1.00, 1.90 d.d (J = 12.0, 8.2)	34.43	1.10, 1.72	34.58	1.10, 2.05 d.d (J = 12.5, 8.4)
23	28.04	0.96 s	28.05	0.98 s	28.04	0.97 s
24	15.43	0.77 s	15.44	0.77 s	15.44	0.77 s
25	16.13	0.82 s	16.04	0.84 s	16.15	0.83 s
26	15.99	1.00 s	16.15	1.02 s	16.00	1.01 s
27	14.81	1.00 s	14.64	0.97 s	14.81	1.00 s
28	60.37	3.20 d (J = 10.4), 3.72 d (J = 10.4)	62.19	3.75 d (J = 11.0), 4.25 d (J = 11.0)	46.32	3.15 d (J = 11.0), 3.60 d.d (J = 11.0, 1.6)
29	36.66	1.32	36.68	1.32	36.64	1.30
30	17.51	1.25	17.56	1.25	17.57	1.24
31	69.75		69.52		69.53	
OC(O)			161.47	8.00 s		

Table 2. ^{13}C and ^{1}H chemical shifts (δ, δ_C, ppm) and coupling constants (J_{HH}) in the NMR spectra of compounds **Va**, **Vb**, **VI**, **VII**, and **IX**

Atom no.	Va		Vb		VI		VII		IX	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
1	38.44	1.00, 1.68	38.54	1.00, 1.68	38.46	1.00, 1.65	38.91	0.94, 1.65	39.86	1.52, 1.91
2	23.73	1.58	23.73	1.58	23.72	1.63	27.41	1.60	34.17	2.37
3	80.93	4.42 d.d (J = 5.6, 10.0)	80.93	4.15 d.d (J = 5.6, 10.0)	80.92	4.40 d.d (J = 5.6, 11.0)	79.00	3.20 d (J = 11.0)	218.11	
4	37.82		37.82		37.84		38.78		47.38	
5	55.38	0.78	55.43	0.75	55.40	0.70	55.40	0.67	55.12	
6	18.24	1.31, 1.48	18.23	1.31, 1.48	18.22	1.49	18.36	1.30, 1.57	19.66	1.33, 1.50
7	34.15	1.36	34.15	1.36	34.19	1.40	34.29	1.37	33.11	1.45
8	40.97		41.04		40.98		41.00		40.57	
9	50.08	1.32	50.61	1.29	50.09	1.32	50.20	1.35	50.70	1.50
10	37.07		37.15		37.08		37.17		37.07	
11	20.89	1.24, 1.48	21.27	1.35, 1.65	20.89	1.22, 1.48	20.94	1.22, 1.47	21.86	2.00
12	28.02	1.62, 2.31	27.60	1.69, 2.32	27.75	1.60, 2.40	27.78	1.60, 2.45	27.00	1.99
13	36.74	1.60	37.07	1.68	36.74	1.63	36.51	1.57	44.10	1.40
14	43.02		42.90		43.06		43.06		40.89	
15	26.75	1.50	27.22	1.50	26.86	1.20, 1.40	26.99	1.40, 1.50	28.32	1.23
16	30.02	1.25, 1.82 d (J = 10.0)	29.76	1.40, 1.80	30.09	1.28, 1.83	29.34	1.22, 1.90	29.72	2.12
17	46.57		46.88		46.67		48.15		93.00	
18	49.92	1.60	48.19	1.48	50.40	1.60	50.38	1.60	49.95	2.00
19	46.88	1.60	43.21	1.95	48.37	1.68	48.43	1.63	48.06	2.05
20	34.87		34.00		33.98		34.03		34.50	
21	26.87	1.00, 1.60	24.96	1.30, 1.90	26.92	1.03, 1.64	26.83	1.05, 1.60	29.02	1.65
22	34.50	1.04, 1.81	32.96	1.01, 1.68	34.48	1.06, 1.87	33.77	1.00, 1.90	33.91	1.40, 2.48
23	28.02	0.80 s	27.99	0.80 s	28.00	0.84 s	28.04	0.95 s	26.86	1.09 s
24	16.55	0.79 s	16.55	0.79 s	16.55	0.83 s	15.43	0.75 s	21.04	1.05 s
25	16.17	0.82 s	16.27	0.82 s	16.21	0.85 s	16.13	0.80 s	15.48	0.97 s
26	16.04	0.99 s	16.17	0.99 s	16.17	1.02 s	16.00	1.00 s	16.33	1.07 s
27	14.77	0.95 s	15.23	0.97 s	14.78	0.98 s	14.13	0.99 s	15.96	0.94 s
28	62.80	3.66 d (J = 11.0), 4.18 d (J = 11.0)	63.06	3.77 d (J = 11.0), 4.17 d (J = 11.0)	62.84	3.60 d (J = 11.0), 4.12 d (J = 11.0)	60.37	3.30 d (J = 11.0), 3.80 d (J = 11.0)		
29	36.66	1.28	32.96	1.15, 1.35	37.11		37.17	1.35	33.19	1.27
30	17.51	1.20 s	18.73	1.22 s	19.96	1.23 s	19.93	1.25	20.16	1.32 s
31	69.56		70.43		41.35		41.65		70.03	
3-OAc	21.38, 171.08	2.00 s	21.38, 171.08	2.00 s	21.37, 171.07	2.06 s				
28-OAc	21.10, 171.5	2.02 s	21.10, 171.58	2.02 s	21.09, 171.55	2.04 s				
17-OAc									22.62, 170.29	2.00 s

Scheme 2.



VIII **IX**

appeared as a triplet at δ_C 62.18 and 46.31 ppm, respectively (Table 1).

Diacetate **Ib** reacted with dichlorocarbene under analogous conditions to give compound **V** in quantitative yield. The product was a mixture of two diastereoisomers at a ratio of 95:5. The major diastereoisomer (**Va**) was isolated by recrystallization, and the minor one (**Vb**) was obtained as a mixture with **Va** at a ratio of 1:1 (according to the ^{13}C NMR spectrum) from the mother liquor. Hydrolysis of the acetate groups in **Va** by the action of a 5% solution of KOH in MeOH afforded diol **II** in quantitative yield. Compounds **Ia** and **Ib** failed to react with diazomethane in diethyl ether in the presence of $Pd(OAc)_2$ [14].

The ^{13}C and ^{1}H NMR spectra of isomer **Vb** were interpreted using the corresponding data for individual stereoisomer **Va**. The chemical shifts of carbon atoms in rings A and B of isomers **Va** and **Vb** differ only slightly ($\Delta\delta_C^{max}$ = 0.1 ppm); the difference in the chemical shifts of carbon atoms in rings C and D reaches 0.5 ppm (for C^{15}). Characteristic are signals from carbon atoms in the cyclopropane ring and ring E. The C^{21}, C^{22}, and C^{29} nuclei in the minor isomer resonate in a stronger field ($\Delta\delta_C$ = 2 ppm; 3.6 ppm for C^{19}) relative to the corresponding signals of the major isomer. Signals from protons on C^{18} and C^{22} also appear in a stronger field, while those from protons on C^{19} and C^{22}, as well as from methyl protons on C^{27} and C^{30}, are displaced downfield by about 0.3 ppm. Diastereotopic protons on C^{29} in the major isomer are equivalent, whereas the chemical shifts of the corresponding protons in the minor isomer differ by 0.2 ppm (Table 2).

Replacement of dichlorocarbene by less electrophilic dibromocarbene leads to increase in the reaction time. Dibromocyclopropane derivative **VI**, which was isolated by column chromatography on silica gel, contained ~20% of impurities which could not be removed by recrystallization. Hydrolysis of diacetate **VI** under the same conditions as in the hydrolysis of **Va** gave diol **VII**. In the ^{13}C NMR spectra of compounds **VI** and **VII**, the C^{31} signal appeared in a considerably stronger field (δ_C 41.35 and 41.65 ppm, respectively), as compared to dichlorocyclopropane derivatives **II** and **III**–**V**.

By reaction of 17-acetoxy-28-norlupan-3-one (**VIII**) with dichlorocarbene we obtained 30% of dichlorocyclopropane derivative **IX** (Scheme 2) together with a considerable amount of unidentified products. The ^{1}H and ^{13}C NMR spectra of **IX** were fully consistent with the assumed structure. In the mass spectrum of **IX**, the most abundant ion was that with *m*/*z* 490.276; it is formed by elimination of AcOH from the molecular ion.

Thus we have synthesized in high yields previously unknown triterpenoids of the lupane series, which contain *gem*-dichloro- and *gem*-dibromocyclopropane fragments in the side chain. These compounds can be used as intermediate products in further transformations of lupane triterpenoids and as potential biologically active substances for studying structure–activity correlations.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM spectrometer (75 MHz for ^{13}C) in chloroform-*d* at room temperature. The chemical shifts were measured relative to the solvent signals (δ 7.27 and δ_C 77.1 ppm). The ^{13}C signals were assigned using JMOD and heteronuclear correlation techniques. The mass spectra (electron impact, 70 eV) were obtained on a Thermo Finnigan MAT 95XP spectrometer with direct sample admission into the ion source; the temperature of the direct inlet probe was programmed from 50 to 270°C at a rate of 25 deg/min. The optical

rotations were measured on a Perkin–Elmer-141 polarimeter. KSM silica gel (100–160 mesh, Russia) was used for column chromatography; thin-layer chromatography was performed using Sorbfil plates (*Sorbpolimer* Ltd., Krasnodar, Russia).

Betulin (**Ia**) was isolated from birch bark according to the procedure described in [15], mp 258–260°C (from methanol); published data: mp 251–252°C. The ^{1}H and ^{13}C NMR spectra of **Ia** were consistent with those given in [8]. Diacetate **Ib** was synthesized by acetylation of betulin (**Ia**) with acetic anhydride in pyridine according to the procedure described in [16], mp 223°C; published data: mp 223–224°C. 17-Acetoxy-28-norlupan-3-one (**VIII**) was synthesized by oxidative decarboxylation of betulonic acid with $Pb(OAc)_4$–pyridine in benzene [17], mp 186–187°C (from pentane), $[\alpha]_D^{20}$ = +42° (*c* = 17, $CHCl_3$). The ^{13}C and ^{1}H NMR spectra of compounds **II**–**VII**, and **IX** are given in Tables 1 and 2.

Reaction of betulin (Ia) with dichlorocarbene. A mixture of 0.50 g (1.12 mmol) of compound **Ia**, 15 ml of chloroform, 5 ml of 50% aqueous sodium hydroxide, and 2.5 mg (0.012 mmol) of benzyltriethylammonium chloride was vigorously stirred for 2 h at 20°C. Water, 10 ml, was added, and the organic phase was separated, washed with water, dried over $MgSO_4$, and evaporated, and the residue was subjected to chromatography on silica gel using benzene–ethyl acetate (75:1) as eluent. We isolated 0.07 g of a complex mixture of unidentified products, 0.16 g of a mixture of 3β-hydroxy-20,29-dichloromethanolupan-28-yl formate (**III**) and 28-chloro-20,29-dichloromethanolupan-3β-ol (**IV**) at a ratio of 4:5 (according to the ^{1}H NMR data), and 0.32 g (55%) of 20,29-dichloromethanolupane-3β,28-diol (**II**). mp 222–223°C (from CCl_4), $[\alpha]_D^{25}$ = –9° (*c* = 1, $CHCl_3$). High-resolution mass spectrum: *m*/*z* 524.318 $[M]^+$. $C_{31}H_{50}Cl_2O_2$. Calculated: *M* 524.318.

Hydrolysis of compound III. A mixture of compounds **III** and **IV** (~4:5), 0.05 g, was added to 8 ml of a 5% solution of potassium hydroxide in methanol, and the mixture was stirred for 12 h at 20°C. The mixture was adjusted to pH 6 by adding 5% hydrochloric acid and filtered, methanol was distilled off from the filtrate on a rotary evaporator, and the remaining aqueous solution was shaken with chloroform. The organic layer was separated, dried over $MgSO_4$, and evaporated, and the residue was subjected to chromatography on silica gel using benzene–ethyl acetate (100:1) as eluent to isolate 0.027 g (96%) of chloride **IV** and 0.015 g (72%) of diol **II**.

Compound **IV**. $[\alpha]_D^{25}$ = –11° (*c* = 3.8, benzene). High-resolution mass spectrum: *m*/*z* 542.286 $[M]^+$. $C_{31}H_{49}Cl_3O$. Calculated: *M* 542.284.

3β,28-Diacetoxy-20,29-dichloromethanolupane (Va/Vb). A mixture of 0.1 g (0.190 mmol) of diacetate **Ib**, 3 ml of chloroform, 1.0 ml of 50% aqueous sodium hydroxide, and 4 mg (0.018 mmol) of benzyltriethylammonium chloride was vigorously stirred for 2.5 h at 20°C. The mixture was diluted with 10 ml of water, and the organic phase was separated, washed with water, dried over $MgSO_4$, and evaporated. The residue was 0.114 g (99%) of a mixture of diastereoisomers **Va** and **Vb** as an oily material. Pentane, 4 ml, was added to the oily residue, the solution was separated from the precipitate by decanting, and the precipitate was washed with pentane (3×1.5 ml) and dried under reduced pressure to obtain 0.10 g (86%) of diacetate **Va**. The filtrate was evaporated, pentane was added to the oily residue, the solution was separated from the precipitate by decanting, and the solvent was removed to obtain 0.01 g (9%) of a mixture of diastereoisomers **Va** and **Vb** at a ratio of 1:1 (according to the ^{13}C NMR data). Oily substance, $[\alpha]_D^{25}$ = +7° (*c* = 1, $CHCl_3$).

Compound **Va**. mp 242–243°C, $[\alpha]_D^{25}$ = +1° (*c* = 2.5, $CHCl_3$). High-resolution mass spectrum: *m*/*z* 549.326 $[M - AcOH]^+$. $C_{33}H_{51}Cl_2O_2$. Calculated: [*M* – AcOH] 549.363.

Hydrolysis of diacetate Va. A mixture of 0.05 g (0.082 mmol) of compound **Va** and 8 ml of a 5% solution of potassium hydroxide in methanol was stirred for 7 h at 20°C. The mixture was left overnight, 5% hydrochloric acid was added to pH 6, the mixture was filtered, methanol was distilled off from the filtrate, the residue was extracted with chloroform, and the extract was dried over $MgSO_4$ and evaporated. The residue was 0.045 g (99%) of diol **II**.

3β,28-Diacetoxy-20,29-dibromomethanolupane (VI). A mixture of 0.10 g (0.19 mmol) of diacetate **Ib**, 2.0 ml of bromoform, 1.0 ml of 50% aqueous sodium hydroxide, and 5 mg (0.022 mmol) of benzyltriethylammonium chloride was vigorously stirred for 5 h at 20°C. The mixture was left overnight, 10 ml of water was added, the mixture was extracted with 10 ml of methylene chloride, the organic layer was separated, washed with water to pH 6, dried over $MgSO_4$, and concentrated, the solvent and excess $CHBr_3$ were removed under reduced pressure, and the residue was subjected to chromatography on silica gel using benzene as eluent. We isolated 0.10 g of compound **VI**

which contained about 20% of impurities (according to the ^{13}C NMR data).

20,29-Dibromomethanolupane-3β,28-diol (VII). A mixture of 0.07 g (0.10 mmol) of compound **VI** and 10 ml of a 5% solution of potassium hydroxide in methanol was stirred for 2 h at 20°C. The mixture was then treated as described above for diacetate **Va**. After removal of the solvent, the residue was subjected to chromatography on silica gel using benzene–ethyl acetate (50:1) as eluent. We isolated 0.45 g (75%) of compound **VII** as an amorphous substance, $[\alpha]_D^{25} = -7°$ (c = 1.2, $CHCl_3$). High-resolution mass spectrum: m/z 612.217 $[M]^+$. $C_{31}H_{50}Br_2O_2$. Calculated: M^+ 612.217.

17-Acetoxy-20,29-dichloromethano-28-norlupan-3-one (IX). A mixture of 0.05 g (0.11 mmol) of compound **VIII**, 2.0 ml of chloroform, 0.5 ml of 50% aqueous sodium hydroxide, and 2.5 mg (0.011 mmol) of benzyltriethylammonium chloride was stirred for 12 h at 20°C. The mixture was left to stand for 48 h and was then treated as described above. After removal of the solvent, the oily residue was subjected to chromatography on silica gel using benzene as eluent to isolate 0.017 g (30%) of acetate **IX** as an amorphous substance, $[\alpha]_D^{25} = +31°$ (c = 0.2, $CHCl_3$). High-resolution mass spectrum: m/z 490.276 $[M - AcOH]^+$. $C_{30}H_{44}Cl_2O$. Calculated: $[M - AcOH]$ 490.276.

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