12.8 Hz, 6-H-exo), 1.58 (d, 1H, ^2J = 9.6 Hz, 7-H-anti), 1.65 (d, 1H, ^3J = 4.5 Hz, 4-H), 1.82 (d, 1H, ^2J = 9.6 Hz, 7-H-syn), 1.91 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.07 (dd, 1H, ^2J = 15.6 Hz, ^3J = 4.5 Hz, 3-H-exo), 2.37 (d, 1H, ^2J = 15.6 Hz, 3-H-endo), 6.14 (1H, NH), 6.30 (1H, NH).

N,N'-Diacetyl-2,2-diamino-5-exo-ethylbicyclo[2.2.1]heptane (IV) was obtained from 2.2 g of the ketone (II), 5 ml of acetonitrile, and 5.2 ml of conc. H_2SO_4 with a yield of 1.6 g (42%). mp 207°C. IR spectrum λ_{max}^{KBr}, cm^{-1}): 3400, 3310 (N–H), 2960, 2870 (C–H), 1660 (C=O, amide I), 1550 (NH). Mass spectrum (m/z): 238 (M^+, 30%), 195, 181, 179, 167, 152, 138, 122, 109, 94, 86, 63, 43 (100%). PMR spectrum (δ, ppm, CD_3OD): 0.96 (m, 5H, 5-C_2H_5), 1.19 (m, 1H, 5-H-endo), 1.31 (dd, 1H, ^2J = 13.2 Hz, $^3J_{endo-endo}$ = 9.6 Hz, 6-H-endo), 1.40 (d, 1H, ^2J = 10.8 Hz, 7-H-anti), 1.53 (dd, 1H, ^2J = 13.2 Hz, $^3J_{endo-exo}$ = 3.6 Hz, 6-H-exo), 1.56 (m, 1H, 4-H), 1.58 (d, 1H, ^2J = 10.8 Hz, 7-H-syn), 1.87 (s, 3H, $COCH_3$), 1.90 (s, 3H, $COCH_3$), 1.92 (d, ^2J = 18.0 Hz, 3-H-endo), 2.16 (dd, 1H, ^2J = 18.0 Hz, ^3J = 4.8 Hz, 3-H-exo), 2.82 (br.s, 1H, 1-H).

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RETRO-MICHAEL REACTION OF 28-METHOXY-18,19-SECOLUPANE-18,19-DIONE DERIVATIVES

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The interactions with KOH in boiling diethyleneglycol of 3β,28-dimethoxy- and 3β-acetoxy-28-methoxy-18,19-secolupane-18,19-diones have been studied. In the first case, 3β-methoxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupan-18-one and the corresponding 18-ol were isolated from the mixture of products, and in the second case 3β-hydroxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupan-18-one – which was also obtained by an analogous reaction from 3β-acetoxy-18,19-secolupan-18,19-dione – and 3β-hydroxy-19,20,21,22,28,29,30-heptanor-18,19-secolupan-18-one. Thus, it has been found that in this case the retro-Michael reaction is accompanied by 28-demethoxylation and partially by 28-demethoxymethylation.

The retro-Michael reaction of triterpene 1,5-diones, which takes place when they are boiled with KOH in diethyleneglycol, has been used in structural investigations and, in particular, in the refinement of the structures of 3-acetoxy-13,17-secodammarane-13,17-dione [1] and of 6-acetoxy-17,21-secozeorinane-17,21-dione [2]. Then, taking 4,5-secolupan-3,5-dione as an example, it was found that an analogous cleavage took place on vacuum distillation with an alkaline glass fractionating column and that under these conditions the yield of de-A-(10βH)lupan-5-one was almost twice as great as the yield of the de-A-(10βH)lupan-5-ol formed on reaction with KOH in diethyleneglycol [3]. In 1986 it was found that the retro-

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TABLE 1. PMR Spectra of the Substituted 18,19-Secolupan-18,19-diones (I-III), the 19,20,21,22,29,30-Hexanor-18,19-secolupanes (IV-VI), and 3β-Acetoxy-19,20,21,22,28,29,30-heptanor-18,19-secolupan-18-one (VII)

Compound	Chemical shifts (δ, ppm)			
	Me-23s-Me27 c (5 Me)	CH_2-28 dd or Me-28 s/d	Me-29, Me-30	H-3α m
I	0,750, 0,790, 8,879, 0,954, 1,121	3,294, 3,664	1,086	2,654
II	0,793, 0,850 (6H), 0,906, 1,126	3,295, 3,655	1,088	4,480
III	0,783, 0,850 (6H), 0,905, 1,110	1,082 s (3H)	1,139	4,483
IV	0,751, 0,781, 0,875, 0,954, 1,104	0,980 d (3H)	—	2,648
V	0,746, 0,832, 0,950, 0,957, 1,071	0,803 d (3H)	—	2,639
VI	0,782, 0,847 (6H), 0,900, 1,109	0,982 d (3H)	—	4,478
VII	0,833, 0,846, 0,851, 0,900, 1,109	—	—	4,480

Compound	Chemical shifts (δ, ppm)		SSCC, Hz		
	R_1(Me)	other H's	$J_{20,29}$, $J_{20,30}$	ΣJ_3	J_{28}
I	3,357	1,2—1,9, 2,5—2,7, 3,267 (3H, R_2)	7,0	16	9,2
II	2,046	1,1—1,9, 2,4—2,7, 3,268 (3H, R_2)	7,5	16,8	9,2
III	2,050	1,2—1,8, 2,500 m (2H), 2,642 m (H-20), 2,725 dd (H-13)	7,6	16	—
IV	3,359	1,1—2,1, 2,280 (J=12, J=6,5, J=6 Hz H-17), 2,490 (J=12, J=4 Hz H-13)	—	16	6,5
V	3,365	1,2—1,9, 2,062 (Ac), 5,002 (H-18)	—	16,2	6,5
VI	2,048	1,0—2,0 2,294 (J=13, J=6,5, J=6 Hz H-17), 2,482 (J=12, J=4 Hz H-13)	—	16	6,5
VII	2,249	1,1—2,0, 2,28 m (2H, H-17), 2,485 dd (J=12, J=4 Hz H-13)		16	

Michael reaction takes place most effectively on the distillation of 1,5-diones with superheated steam through a column with a basic catalyst deposited on glass wool and heated to 200-280°C. Thus, when NaOH was used as the catalyst, 1,5-diones (13,17-secodammarane-13,17-dione, 17,21-secogonane-17,21-dione, and 4,5-secolupan-3,5-dione) gave the corresponding monoketones with yields of 85-100% [4].

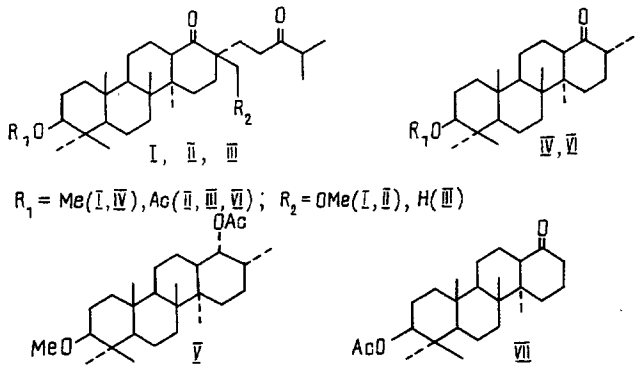
Here we present the results of an investigation of the retro-Michael reaction of 18,19-secolupan-18,19-dione derivatives performed with the aim of obtaining 19,20,21,22,28,29,30-heptanor-18,19-secolupan-18-one as a possible synthon for the synthesis of natural D-homodammarane derivatives. It was impossible to achieve the required cleavage of 3β,28-diacetoxy-18,19-secolupan-18,19-dione because of the competing processes of hydrolysis and a retro-aldol reaction taking place under milder conditions and giving a 28-nor derivative not participating in the retro-Michael reaction. We therefore obtained for study the previously undescribed 3β,28-dimethoxy-18,19-secolupan-18,19-dione (I) and 3β-acetoxy-28-methoxy-18,19-secolupan-18,19-dione (II) and also the known 3β-acetoxy-18,19-secolupan-18,19-dione (III) [7] by the oxidation with ruthenium tetroxide of the corresponding 18-lupene derivatives that had been obtained from betulin and lupeol.

An attempt to perform the retro-Michael reaction with dione (I) in the vapor phase by the procedure of [4] was unsuccessful because dione (I) did not distill with superheated steam. The reaction was therefore carried out under the usual conditions [2, 3] by boiling with KOH in diethyleneglycol in an Ar atmosphere. The dione (I) then gave a mixture of products from which two compounds were isolated by preparative TLC: 3β-methoxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupan-18-one (IV) and the corresponding 18-ol, characterized as the 18-acetate (V), the structures of which were established on the basis of their IR and mass spectra and their PMR (Table 1) and ^{13}C NMR (Table 2) spectra. The similar reaction of dione (II) gave a mixture of products from which, after acetylation, TLC permitted the isolation of 3β-acetoxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupan-18-one (VI) and, with half the yield of this, 3β-acetoxy-19,20,21,22,28,29,30-heptanor-18,19-secolupan-18-one (VII).

TABLE 2. ^{13}C NMR Chemical Shifts of the Substituted 18,19-Secolupan-18,19-diones (I-III), the 19,20,21,22,29,30-Hexanor-18,19-secolupanes (IV-VI), and 3β-Acetoxy-19,20,21,22,28,29,30-heptanor-18,19-secolupan-18-one (VII) (δ, ppm)

C atom	I	II	III	IV	V	VI	VII
1	39,0	38,8	38,8	39,0	39,0	38,8	38,3
2	22,4	23,8	23,8	22,5	22,5	23,8	23,8
3	88,6	80,7	80,8	88,6	88,8	80,8	80,8
4	39,0	37,8	38,0	39,0	39,0	38,0	37,9
5	56,3	55,7	55,8	56,3	56,3	55,7	55,7
6	18,5	18,4	18,4	18,4	18,4	18,4	18,4
7	34,4	34,3	34,2	34,5	33,7	34,4	34,4
8	41,2	41,2	41,2	41,1	41,3	41,1	41,0
9	51,1	50,9	51,0	51,1	51,0	51,1	51,0
10	37,5	37,3	37,4	37,5	37,5	37,4	37,4
11	20,1	20,1	20,2	20,1	21,1	20,1	20,0
12	22,3	22,2	22,3	22,2	26,2	22,2	22,0
13	49,4	49,4	48,0	52,4	41,5	52,3	52,6
14	46,4	46,3	46,6	47,1	40,5	47,1	46,3
15	27,3	27,2	27,0	31,2	31,4	31,3	31,1
16	29,2	29,2	32,5	32,2	26,3	32,2	22,7
17	51,3	51,3	46,5	44,7	36,1	44,7	41,2
18	214,6	214,4	214,5	214,5	77,1	214,4	213,6
19	214,6	214,4	216,9	—	—	—	—
20	40,8	40,7	40,9	—	—	—	—
21	35,7	35,7	35,7	—	—	—	—
22	30,4	30,3	34,2	—	—	—	—
23	28,2	28,0	28,1	28,1	28,2	28,1	28,0
24	16,7	16,7	16,8	16,7	16,3	16,8	16,8
25	16,2*	16,4*	16,1*	16,3*	16,2*	16,2*	16,2*
26	16,4*	16,6*	16,6*	16,2*	16,1*	16,6*	16,6*
27	16,2*	16,1*	16,1*	14,5	15,6	14,5	16,1*
28	77,6	77,7	24,3	16,1*	17,7	16,1*	—
29, 30	18,4	18,3	18,4	—	—	—	—
R_1: 1′	57,5	170,5	170,6	57,5	57,4	170,8	170,6
2′	—	21,2	21,2	—	—	21,3	21,3
R_2	59,4	59,3	—	—	—	—	—
AcO—18: 1″	—	—	—	—	170,6	—	—
2″	—	—	—	—	20,9	—	—

*Assignment of the signals ambiguous.



For a direct confirmation of the 28-demethoxylation that we had detected in the course of the retro-Michael reaction of diones (I) and (II) in place of the expected 28-demethoxymethylation, we performed this reaction with dione (III), in which a 28-methyl group was initially present. From the acetylated mixture of products we isolated a sample of the ketone (VI), identical in terms of melting point and PMR spectrum with that obtained from the dione (II). The 28-methyl group in ketone (VI) had the equatorial α configuration, as followed from the nature of the signal of the resonance of the H-17 proton, the multiplet of which at 2.294 ppm was converted after the suppression of spin-spin coupling with Me-28α, 0.982 ppm (d, J = 6.5 Hz), into a doublet of doublets with J = 13 and 6 Hz corresponding to an axial H-17β. The configuration of the C-13 center with an axial H-13β had not changed,

as followed from the form of its PMR signal at 2.482 ppm (dd, J = 12 and 4 Hz). The same applies to ketone (IV) (see Table 1). It is impossible to say anything definite about the configurations of H-13 and H-17 in compound (V) from its PMR spectrum, since the resonance signals of these protons lay in the 1.2-1.9 ppm region together with others. However, the H-18 signal at 5.002 ppm, having the form of an almost regular triplet with an apparent J = 2.9 Hz, indicated, on the one hand, its equatorial β-orientation and, on the other hand, apparently, the same positioning of H-13 and H-17 relative to H-18 and, consequently, their β-orientation, since it seems unlikely that both these protons changed their configuration on the reduction of the 18-keto group to an alcohol group during the retroreaction. The PMR spectrum of ketone (VII) (see Table 1) contained the singlet signals of the resonance of only 5 skeletal Me groups in the 0.8-1.1 ppm region, an H-13β signal at 2.485 ppm (dd, J = 12 and 4 Hz), and a CH_2 multiplet of H-17 at 2.28 ppm.

In the ^{13}C NMR spectra of compounds (IV-VII), as compared with those of compounds (I-III) (see Table 2), correspondingly smaller numbers of resonance signals of C atoms were observed, together with changes in the chemical shifts of the C-17 and C-18 atoms the functional groups attached to which had changed.

The compounds (IV-VII) that have been obtained may be of interest as synthons, for example, in the production of hitherto unknown representatives of the D-homodammarane series.

EXPERIMENTAL

IR spectra were taken on a Specord 75-IR instrument for solutions in $CHCl_3$. PMR spectra were obtained on a Bruker WM-250 spectrometer at working frequencies of 250 MHz for ^1H and 62.9 MHz for ^{13}C at 30°C for solutions in $CDCl_3$. CSs are expressed on the δ scale relative to TMS. The accuracy of the measurements was ±0.15 Hz for ^1H and ±1.9 Hz for ^{13}C. Mass spectra were recorded on an LKB 9000S instrument with a system for the direct introduction of the sample into the ion source at energies of the ionizing electrons of 15 and 70 eV. The melting points of the substances were determined on a Boëtius stage. Optical rotations were measured on a Perkin–Elmer 141 polarimeter in cells 10 cm long with solutions in $CHCl_3$.

The course of the reactions and the purity of the compounds were monitored by TLC on Silufol 25 × 75 cm plates (Czechoslovakia) in the hexane–acetone (3:1) system. The TLC plates were visualized by brief immersion in a saturated solution of $SbCl_3$ in $CHCl_3$ followed by heating at 120°C for 1-3 minutes. Preparative TLC was conducted on 20 × 20 cm glass plates with an unfixed layer of Silpearl (Czechoslovakia) 1 mm thick in the hexane–acetone (3:1) system, with visualization by means of iodine. The colored zones were taken off and were extracted with $CHCl_3$. To eliminate iodine the extracts were stirred with slightly moistened crystals of $Na_2S_2O_3$ and were dried over anhydrous Na_2SO_4 and evaporated to dryness in a rotary evaporator under the vacuum of a water-jet pump. The products were recrystallized from ethanol. The elementary analyses of the new compounds corresponded to the calculated values.

The starting compounds, 3β,28-diacetoxy-18-lupene (VIII) and 3β,28-dihydroxy-18-lupene (IX), were obtained by the procedure of [5]. Methylation of the diol (IX) was achieved in a similar way to that described for betulin [8], with a change only in the procedure for isolating the product. 3β-Acetoxy-18-lupene (X) was obtained by the isomerization of lupeol acetate [9].

3β,28-Dimethoxy-18-lupene (XI). A flask fitted with a magnetic stirrer with heater, a dropping funnel, a reflux condenser with $CaCl_2$ tube, a thermometer, and a tube for the passage of gas was charged with 2.0 g (41.7 mmole) of NaH and 80 ml of absolute THF. While the suspension of NaH in THF was being stirred in an atmosphere of dry Ar at 45-50°C, 5.50 g (12.4 mmole) of the diol (IX) and 12 ml (193 mmole) of MeI in 40 ml of THF were added over one hour, and the reaction mixture was stirred at 45-50°C for another 3 h. The mixture was cooled and filtered, treated with 5 ml of EtOH, evaporated almost to dryness, and diluted with water. The precipitate was filtered off, washed with water to neutrality, and dried in vacuum. This gave 5.68 g (93.7%) of the ether (XI), homogeneous according to TLC, mp 193-195°C (MeOH): $[\alpha]_{578}^{20}$ −4.9° (c 0.020). PMR: 2.652 (1H, q, J = 11.5 Hz, J = 4.2 Hz, H-3α), 3.056 (1H, d, J = 9.5 Hz, H-28), 3.125 (1H, m, J = 6.8 Hz, H-20), 3.346 (3H, s, MeO-28), 3.363 (3H, s, MeO-3), 3.398 (1H, d, J = 9.5 Hz, H-28). ^{13}C NMR: 75.43 (C-28), 88.62 (C-3), 135.26 (C-18), 142.22 (C-19).

3β-Acetoxy-28-hydroxy-18-lupene (XII). A solution of 10.140 g (19.25 mmole) of the diacetate (VIII) and 2.0 g (36 mmole) of KOH in a mixture of 150 ml of EtOH and 150 ml of C_6H_6 was stirred at 20°C for 5 h and was then treated with KU-2-8 cation-exchange resin, filtered, and evaporated to dryness. The residue was transferred to a column of silica gel L 100-160 μm (Czechoslovakia), and elution with hexane–acetone (20:1) gave the initial diacetate (VIII) and with hexane–acetone (18:1) the monoacetate (XII). The yield of (XII) was 5.0 g (53.6%), mp 238-242°C (EtOH); $[\alpha]_{578}^{20}$ −9.0° (c 0.012). IR spectrum, ν_{max}, cm^{-1}: 3614, 3538 (OH), 1720 (C=O). PMR: 2.050 (3H, s, AcO-3), 3.193 (1H, m, J = 6.8 Hz, H-20), 3.335 (1H, d, J = 11 Hz, H-28) and 3.666 (1H, m, J = 11 Hz, H-28), 4.484 (1H, m, ΣJ = 16.2 Hz, H-3α). ^{13}C NMR: 66.44 (C-28), 80.89 (C-3), 133.79 (C-18), 144.72 (C-19), 170.54 (OCO-3).

3β-Acetoxy-28-methoxy-18-lupene (XIII). A flask fitted with a magnetic stirrer having a Teflon rotor was charged with 2.00 g (4.12 mmole) of (XII), 50 ml of CH_2Cl_2, and 0.1 ml of $BF_3 \cdot Et_2O$. The flask was closed with a cork stopper fitted with a $CaCl_2$ tube and a tube reaching almost to the bottom, through which was passed the CH_2N_2 distilled off from an ethereal solution obtained according to [10] from 35 g (163 mmole) of N-methyl-N-nitroso-p-toluenesulfonamide. The reaction mixture was filtered and evaporated to dryness. The residue, containing (according to GLC), 97% of the desired product and 3% of the monoacetate (XII), was recrystallized from EtOH. This gave 1.37 g (66.6%) of the ester (XIII), mp 232-234°C; $[\alpha]_{578}^{20}$ −13.5° (c 0.010). Mass spectrum, m/z (%): 498 (M^+, 48). PMR: 2.045 (3H, s, AcO-3), 3.058 (1H, d, J = 9.2 Hz, H-28), 3.119 (1H, m, J = 6.8 Hz, H-20), 3.340 (3H, s, MeO-28), 3.394 (1H, d, J = 9.2 Hz, H-28), 4.484 (1H, m, ΣJ = 16.8 Hz, H-3α). ^{13}C NMR: 59.31 (MeO-28), 75.64 (C-28), 80.91 (C-3), 135.20 (C-18), 142.37 (C-19), 170.53 (AcO-3).

The substituted 18,19-secolupane-18,19-diones (I-III) were obtained by the "general procedure for oxidizing triterpenoids with ruthenium tetroxide" [5] from the corresponding 18-lupenes (XI), (XII), and (X). The yields of the diones (I-III), recrystallized from EtOH amounted to 70-80%. Details of the PMR spectra of compounds (I-III) are given in Table 1, and of their ^{13}C NMR spectra in Table 2.

3β-28-Dimethoxy-18,19-secolupane-18,19-dione (I). mp 165-170°C; $[\alpha]_{578}^{20}$ +52.2° (c 0.010). Mass spectrum, m/z (%): 502 (M^+, 85), 470(70), 459(40), 457(35), 442(25), 427(22), 404(55), ..., 208(100). IR spectrum, ν_{max}, cm^{-1}: 1704 (C=O).

3β-Acetoxy-28-methoxy-18,19-secolupane-18,19-dione (II). mp 152-153°C; $[\alpha]_{578}^{20}$ +61.9° (c 0.035). Mass spectrum, m/z (%): 530 (M^+, 57), 498(64), 488(37), 471(52), 433(66), 427(75), ..., 67(100). IR spectrum, ν_{max}, cm^{-1}: 1708 (C=O).

3β-Acetoxy-18,19-secolupane-18,19-dione (III). mp 176-181°C; $[\alpha]_{578}^{20}$ +51.7° (c 0.014). Literature [7]: mp 188-189° (MeOH); $[\alpha]_D$ +39°.

Interaction of the Diones (I-III) with KOH in Diethyleneglycol. To a solution of 0.6 g of KOH in 30 ml of anhydrous diethyleneglycol being boiled in an atmosphere of Ar was added 500 mg (1 mmole) of one of the diones (I-III) and the mixture was boiled for 1 h under Ar. The cooled reaction mixture was poured into water, neutralized with 10% H_2SO_4, and extracted with $CHCl_3$. The extract was washed with water, dried with Na_2SO_4, and evaporated to dryness. In the case of dione (I), the residue was subjected to preparative TLC, and two main products were isolated. The less polar product was recrystallized from EtOH, to give 111 mg (30%) of the ketone (IV). The more polar product was acetylated with Ac_2O–Py, and, after recrystallization from EtOH, 50 mg (12%) of the ester (V) was obtained. In the cases of the diones (II) and (III), the residue was acetylated with Ac_2O–Py and the products were isolated by preparative TLC. Dione (II) gave 80 mg (21%) of ketone (VI) and 86 mg of a more polar product from which, by further TLC, was isolated 120 mg (30%) of compound (VI), identical in melting point and NMR spectra with the sample obtained from dione (II).

3β-Methoxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupan-18-one (IV). mp 201-205°C; $[\alpha]_{578}^{20}$ +30.3° (c 0.020). Mass spectrum, m/z (%): 374 (M^+, 10), 342(4), 327(4), 303(4), 248(3), 221(14). IR spectrum, ν_{max}, cm^{-1}: 1698 (C=O).

18α-Acetoxy-3β-methoxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupane (V). mp 194-199°C. $[\alpha]_{578}^{20}$ +59.7° (c 0.012). Mass spectrum, m/z: 418 (M^+), 396, 358, 342, 325, 310, 282, ... IR Spectrum, ν_{max}, cm^{-1}: 1720 (C=O).

3β-Acetoxy-19,20,21,22,29,30-hexanor-18,19-seco(17βH)lupan-18-one (VI). mp 183-186°C; $[\alpha]_{578}^{20}$ +23.8° (c 0.026). Mass spectrum, m/z (%): 402 (M^+, 10), 384(3), 372(2), 354(3),

342 ([m = M^+–AcOH], 22), 327(11), 298(13), 291 ([m* = m^2/M^+], 3), 264(8), ..., 149(100). IR spectrum, ν_{max}, cm^{-1}: 1718 (C=O).

3β-Acetoxy-19,20,21,22,28,29,30-heptanor-18,19-seco(17βH)lupan-18-one (VII). mp 200-203°C; $[\alpha]_{578}^{20}$ +22.0° (c 0.012). Mass spectrum, m/z (%): 388 (M^+, 6), 373(1), 370(3), 332(3), 327(15), 313(7), 285(9), 284(9), 276(6), 264(10), 265(25), 213(11), 204(16), 189(54), 166(79), 151(100), 111(67), 97(63), 95(72), 83(100). IR spectrum, ν_{max}, cm^{-1}: 1722, 1704 (C=O).

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CRYSTAL AND MOLECULAR STRUCTURES OF 4-ACETAMIDO-2,6-DIBROMO-4-HYDROXY-1,2-DIMETHOXYCYCLOHEXA-2,5-DIENE

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A complete x-ray investigation has been made of 4-acetamido-2,6-dibromo-4-hydroxy-1,1-dimethoxycyclohexa-2,5-diene, isolated from the marine sponge Verongia gigantea. It has been shown that the orientation of the acetamide group in the molecule is stabilized by an intramolecular O–H...O hydrogen bond with the hydroxy group.

Bromine derivatives of tyrosine are known as products of biosynthesis in marine sponges [1]. 4-Acetamido-2,6-dibromo-4-hydroxy-1,1-dimethoxycyclohexa-2,5-diene (I) was first detected in a methanolic extract of the sponge Verongia fistularis [2]. In the present paper we give the results of an x-ray structural investigation of this compound carried out with the aim of elucidating stereochemical features of compounds of the type of (I) containing a hydroxy group and an acetamido group in position 4 and differing by the substituents in position 1 (keto group, OMe and OEt groups), not all of which crystallize well (see top of following page).

The spatial structure of the (I) molecule is shown in Fig. 1. The cyclohexane ring in (I) is planar. The deviations of the ring atoms from the mean plane passing through all its

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