7-O-ALKENYL AND ALKYNYL DERIVATIVES OF DAUNOMYCINONE

Věra PŘIKRYLOVÁ, Petr SEDMERA, Josef V. JIZBA, Jindřich VOKOUN, Helena LIPAVSKÁ, Miloslav PODOJIL and Zdenko VANĚK

Institute of Microbiology, Czechoslovak Academy of Sciences, 142 20 Prague 4

Received January 14th, 1985

Reaction of daunomycinone (*I*) with unsaturated alcohols and *p*-toluenesulfonic acid produces a mixture of 7(*S*)-O- and 7(*R*)-O-alkenyl or alkynyl derivatives *II*, *III*, *VI*—*XVII*. With daunomycinone and 2-methyl-2-propen-1-ol, the ketals *IV* and *V* are formed.

To improve the biological activity of antitumour anthracycline compounds, they are subjected to chemical conversion. Daunomycine was chemically modified both in aglycone (daunomycinone, *I*) and in sugar parts[1,2]. We have recently prepared daunomycinone derivatives modified at the position 7, 7-O-alkyl derivatives[3]. Some of them inhibit the growth of *B. subtilis*. However, their main disadvantage is the low solubility in hydrophilic solvents and the difficulties with their testing resulting from this property. The preparation of hydrophilic derivatives requires a multistep synthesis in which the 7-O-derivatives are the intermediates. Double bond introduced into the molecule becomes the reaction center for further modifications. This communication deals with the reaction of daunomycinone with unsaturated alcohols.

Two main products are formed in the reaction of daunomycinone (*I*) with the corresponding alcohol and *p*-toluenesulfonic acid under boiling in benzene–xylene mixture. An exception is the reaction of daunomycinone with 1-penten-3-ol, in which four compounds result (Table I). The physical properties of reaction products (Table II) are different enough. Their mass spectra (Table III) exhibit molecular ions of sufficient intensity to permit high resolution determination of molecular formulae. The fragmentation contains ions already described[4] for daunomycinone (*I*). Additional ions *m/z* 363 and 364 (in comparison with 7-O-alkyl derivatives[3]) correspond to rupture of the $C_{(7)}$—O bond. Large intensity of these ions is especially noticeable with compounds *IV* and *V*. ^{1}H NMR spectra of reaction products (Table IV) contain both signals of protons belonging to daunomycinone and to the corresponding unsaturated alcohol, with expected chemical shifts and multiplicities. To place the compound either to the (7*S*) or to the (7*R*) series, it is necessary to determine in which of the two most probable conformations ($^8H_9$ or $^9H_8$) the alicyclic ring of daunomycinone exists. The diagnostic criterion is relative magnitude of chemi-

cal shifts of pseudoaxial and pseudoequatorial methylene group protons. Pseudoequatorial protons $H_{(8e)}$ and $H_{(10e)}$ can be easily identified by their long-range coupling. For conformation $^8H_9$ it holds $\delta H_{(8e)} > \delta H_{(8a)}$ and $\delta H_{(10e)} > \delta H_{(10a)}$; with conformation $^9H_8$ both relations are reversed[3]. The configuration at $C_{(7)}$ is then judged according to the magnitude of coupling constants $J_{7,8a}$ and $J_{7,8e}$ or using the width of the $H_{(7)}$ multiplet that is approximately equal to their sum. This width is 5·5–6·1 Hz for (7*S*) in the conformation $^8H_9$, 14·5–18·0 Hz for (7*R*) in the conformation $^8H_9$, and 8·6–11·0 Hz for (7*R*) in the conformation $^9H_8$ (refs[3,5]). No (7*S*) derivatives existing in the conformation $^9H_8$ have been described yet. Supporting evidence is the chemical shift of the $COCH_3$ protons. Its value is always slightly lower in the pseudoaxial orientation (7*R*, $^9H_8$) then in the usual one (7*S*, $^8H_9$). Also the $C_{(6)}$—OH proton resonates at higher field in the (7*R*, $^9H_8$) series (0·07–0·10 ppm, concentrations 3–30 mg/ml). Using the above described) procedure, compounds *II*, *VI*, *VIII*, *IX*, *XII*, *XIV*, and *XVI* were placed in the (7*S*) series and compounds *III*, *VII*, *X*, *XI*, *XIII*, *XV*, and *XVII* in the (7*R*) series having the conformation $^9H_8$. The differences in the NMR parameters of side chain protons of compounds formed by reaction of daunomycinone with 1-penten-3-ol are small. Therefore, we deduce that these compounds are diastereomers derived from both (*S* and *R*) forms of the alcohol.

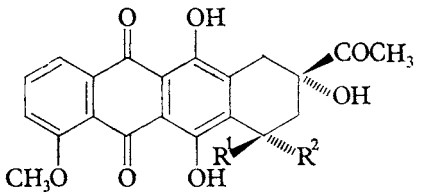
Yields of the reaction of daunomycinone with unsaturated alcohols are quite high under the conditions used. Two compounds, the corresponding (7*S*) and (7*R*) derivatives, are formed in the reaction with 2-propen-1-ol, 4-penten-1-ol, 3-buten-1-ol, *trans*-2-buten-1-ol, and 2-propyn-1-ol. Four compounds result in the reaction of *I* with 1-penten-3-ol; compounds *VIII*, *IX*, *X*, and *XI* are probably diastereomers

TABLE I
Reaction of daunomycinone with alcohols

Alcohol	Temperature °C	Time h	Yield %	Products	Ratio[a] (7*S*)/(7*R*)
2-Propen-1-ol	120	5	90	*II*, *III*	6·5
2-Methyl-2-propen-1-ol	120	1	69	*IV*, *V*	10·0
4-Penten-1-ol	115	20	88	*VI*, *VII*	4·4
1-Penten-3-ol	115	15	65	*VIII*, *IX*, *X*, *XI*	5·6 : 5·7 : 2 : 1
3-Buten-1-ol	115	9	91	*XII*, *XIII*	3·5
trans-2-Buten-1-ol	115	20	86	*XIV*, *X*	2·8
2-Propyn-1-ol	110	0·5	91	*XVI*, *XVII*	4·4

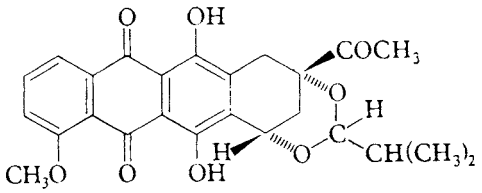
[a] Calculation based on isolated products.

in the (7*S*) and (7*R*) series, respectively. The (7*S*) compounds are preponderant in all cases.



I, $R^1 = H$; $R^2 = OH$
II, $R^1 = H$; $R^2 = OCH_2CH{=}CH_2$
III, $R^1 = OCH_2CH{=}CH_2$; $R^2 = H$
VI, $R^1 = H$; $R^2 = O(CH_2)_3CH{=}CH_2$
VII, $R^1 = O(CH_2)_3CH{=}CH_2$; $R^2 = H$
VIII, *IX*, $R^1 = H$; $R^2 = OCH(CH_2CH_3)(CH{=}CH_2)$
X, *XI*, $R^1 = OCH(CH_2CH_3)(CH{=}CH_2)$; $R^2 = H$

XII, $R^1 = H$; $R^2 = OCH_2CH_2CH{=}CH_2$
XIII, $R^1 = OCH_2CH_2CH{=}CH_2$; $R^2 = H$
XIV, $R^1 = H$; $R^2 = OCH_2CH{=}CHCH_3$
XV, $R^1 = OCH_2CH{=}CHCH_3$; $R^2 = H$
XVI: $R^1 = H$; $R^2 = OCH_2C{\equiv}CH$
XVII, $R^1 = OCH_2C{\equiv}CH$; $R^2 = H$



IV, *V*

The behaviour of compounds *IV* and *V* under electron impact can be understood on the basis of their NMR spectra. Instead of olefinic protons they contain a moiety $O{>}CHCH(CH_3)_2{<}O$, proved by decoupling. Methine proton at 4·58 ppm (4·90 ppm with compound *V*) is directly coupled to a carbon atom δ_C 94·9 (95·8 ppm, respectively). The chemical shift of the later is typical for carbons of the O—CH—O type. Therefore, both compound are 7,9-ketals of daunomycinone and 2-methylpentanal. The alcohol undergoes a double bond rearrangement so that daunomycinone reacts with 2-methylpentanal. Chemical shift differences observed with alkyl side chain protons in compounds *IV* and *V* suggest that these compounds are isomers at $C_{(1')}$. Different conformation of 1,3-dioxane ring cannot be also excluded.

TABLE II

Physical properties of compounds *II*–*XVII*

Compound	M.p., °C	$[\alpha]_{20}^{D}$ (conc.)[a]	R_F[b]	Formula (m.wt.)	Calculated/Found %C	%H
II	86–88	+301 (0·11)	0·59	$C_{24}H_{22}O_8$ (438·4)	65·74 65·59	5·06 5·01
III	208–211	−220 (0·08)	0·43	$C_{24}H_{22}O_8$ (438·4)	65·74 65·80	5·06 5·13
IV	196–198	+437 (0·09)	0·60	$C_{25}H_{24}O_8$ (452·4)	66·36 66·42	5·35 5·40
V	166–168	+182 (0·10)	0·58	$C_{25}H_{24}O_8$ (452·4)	66·36 66·49	5·35 5·39
VI	142–143	+284 (0·10)	0·59	$C_{26}H_{26}O_8$ (466·5)	66·94 66·80	5·62 5·73
VII	159–160	−145 (0·08)	0·46	$C_{26}H_{26}O_8$ (466·5)	66·94 66·82	5·62 5·69
VIII	189–191	− 18 (0·11)	0·60	$C_{26}H_{26}O_8$ (466·5)	66·94 66·85	5·62 5·71
IX	200–202	+ 30 (0·10)	0·60	$C_{26}H_{26}O_8$ (466·5)	66·94 66·99	5·62 5·74
X	221–224	+ 19 (0·09)	0·49	$C_{26}H_{26}O_8$ (466·5)	66·94 66·83	5·62 5·59
XI	197–199	− 45 (0·11)	0·49	$C_{26}H_{26}O_8$ (466·5)	66·94 66·71	5·62 5·73
XII	144–146	+269 (0·10)	0·60	$C_{25}H_{24}O_8$ (452·4)	66·36 55·50	5·35 5·28
XIII	173–176	−173 (0·10)	0·48	$C_{25}H_{24}O_8$ (452·4)	66·36 66·47	5·35 5·42
XIV	89–91	+284 (0·11)	0·59	$C_{25}H_{24}O_8$ (452·4)	66·36 66·41	5·35 5·32
XV	193–195	−169 (0·09)	0·41	$C_{25}H_{24}O_8$ (452·4)	66·36 66·29	5·35 5·43
XVI	112–113	+169 (0·13)	0·51	$C_{24}H_{20}O_8$ (436·4)	66·35 66·22	4·62 4·54
XVII	208–210	− 80 (0·10)	0·41	$C_{24}H_{20}O_8$ (436·4)	66·35 66·30	4·62 4·57

[a] Measured in chloroform; [b] DC Fertigplatten Kieselgel 60 Merck, system benzene–chloroform–ethyl acetate–methanol 7 : 7 : 3 : 1.

TABLE III

Mass spectra of compounds *II*—*XVII*

m/z	Composition[a]	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*[b]	*IX*	*X*	*XI*	*XII*	*XIII*	*XIV*[b]	*XV*	*XVI*	*XVII*
466[c]	$C_{26}H_{26}O_8$	—	—	—	—	16	6	4	7	2	1	—	—	—	—	—	—
452[c]	$C_{25}H_{24}O_8$	—	—	5	11	—	—	—	—	—	—	20	9	2	2	—	—
438[c]	$C_{24}H_{22}O_8$	10	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
436[c]	$C_{24}H_{20}O_8$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	18	7
398	$C_{21}H_{18}O_8$	5	—	—	—	3	—	12	11	—	—	3	—	4	1	1	—
382	$C_{21}H_{18}O_7$	51	29	1	—	20	19	45	85	34	32	13	12	35	45	12	11
380	$C_{21}H_{16}O_7$	6	5	1	—	7	7	6	9	6	5	13	10	4	4	3	4
364	$C_{21}H_{16}O_6$	20	15	71	25	9	9	15	15	15	18	9	6	16	15	5	4
363	$C_{21}H_{15}O_6$	17	12	24	82	17	13	17	15	15	18	15	13	21	14	7	5
362	$C_{21}H_{14}O_6$	63	40	11	8	60	44	51	48	47	50	50	33	77	53	20	18
344	$C_{21}H_{12}O_5$	30	20	6	4	19	17	17	13	14	17	14	10	47	30	4	5
339	$C_{19}H_{15}O_6$	92	84	4	3	49	54	81	100	86	95	31	36	69	100	34	32
338	$C_{19}H_{14}O_6$	34	55	5	8	29	62	28	33	42	42	30	56	17	36	27	46
337	$C_{19}H_{13}O_6$	100	100	14	18	100	100	91	96	100	100	100	100	44	69	100	100
329	$C_{20}H_9O_5$	8	5	3	1	4	3	4	3	3	4	2	3	10	9	—	—
321	$C_{19}H_{13}O_5$	69	63	100	100	43	48	65	79	80	88	33	37	45	67	19	17
319	$C_{19}H_{11}O_5$	33	26	5	6	20	20	18	24	22	26	16	15	21	23	11	11
309	$C_{18}H_{13}O_5$	81	48	20	21	57	33	54	59	42	45	65	36	35	34	54	36
306	$C_{18}H_{10}O_5$	17	18	19	12	11	11	14	14	16	18	10	10	12	16	5	5
301	$C_{19}H_9O_4$	20	15	5	5	12	10	13	11	12	13	10	9	26	16	4	4
217	$C_{12}H_9O_4$	48	34	23	19	31	20	26	29	21	24	28	18	20	19	26	18

[a] Elemental composition of all molecular ions was determined by high-resolution measurement; this measurement on fragments 217—398 was performed with some compounds only; [b] base peak *m/z* 57; [c] molecular ion.

TABLE IV

^{1}H NMR spectra of compounds *II*—*XVII*[a]

Compound	$C_{(6)}$—OH	$C_{(11)}$—OH	7	8a	8e	10a
II	13·94 s	13·27 s	5·06—5·41	1·99 dd (14·7, 3·7)	2·40 ddd (14·7, 2·4, 1·0)	2·93 d (19·5)
III	13·86 s	13·29 s	5·06—5·35	2·55 dd (14·6, 3·7)	2·11 ddd (14·6, 6·1, 1·2)	3·27 d (17·1)
VI	13·94 s	13·29 s	5·02 mt (W = 6·9)	1·96 dd (14·6, 3·7)	2·40 ddd (14·6, 2·4, 1·2)	2·92 d (19·5)
VII	13·84 s	13·31 s	5·08 dd (4·9, 3·7)	2·52 dd (14·6, 4·9)	2·07 ddd (14·6, 3·7, 1·0)	3·23 d (19·4)
VIII	14·05 s	13·33 s	5·10—5·51	1·94 dd (14·7, 3·7)	2·36 dt (14·7, 1·8)	2·95 d (19·5)
IX	13·94s	13·29 s	5·03—5·35	1·88 dd (14·6, 3·7)	2·40 ddd (14·6, 2·4, 1·2)	2·95 d (19·5)
X	13·94 s	13·33 s	5·03—6·06	2·42 dd (14·7, 3·7)	2·06 ddd (14·7, 5·5, 0·8)	3·25 d (18·0)
XI	13·86 s	13·31 s	4·88—6·19	2·52 dd (14·6, 4·9)	2·02 ddd (14·6, 4·9, 1·2)	3·32 d (17·1)
XII	13·96 s	13·31 s	4·92—6·14	1·92 dd (14·7, 4·3)	3·24 ddd (14·7, 2·4, 1·2)	2·97 d (18·9)
XIII	13·86 s	13·31 s	4·86—6·13	2·52 dd (14·7, 3·7)	2·08 ddd (14·7, 5·5, 1·2)	3·23 d (17·1)
XIV	13·96 s	13·30 s	5·10 dd (3·7, 2·4)	1·96 dd (15·6, 3·7)	2·38 ddd (15·6, 2·4, 1·5)	2·95 d (18·6)
XV	13·87 s	13·31 s	5·10 t (4·9)	2·52 dd (14·6, 4·9)	2·07 ddd (14·6, 4·9, 1·2)	3·27 d (17·1)
XVI	13·99 s	13·25 s	5·21 mt (W = 6·3)	2·04 dd (14·6, 3·7)	2·60 ddd (14·6, 2·4, 1·2)	2·94 d (18·9)
XVII	13·92 s	13·29 s	5·22 t (4·9)	2·60 dd (14·6, 4·9)	2·22 ddd (14·6, 4·9, 0·9)	3·27 d (18·9)
IV	13·75 s	13·18 s	5·65 dd (3·7, 1·8)	1·76 dd (12·8, 1·8)	2·33 ddd (12·8, 3·7, 1·2)	3·31 d (20·1)
V	13·81 s	13·24 s	5·57 dd (3·7, 1·8)	1·90 dd (14·4, 1·8)	2·56 ddd (14·4, 3·7, 1·8)	2·84 d (18·3)

[a] Chemical shift, multiplicity, coupling constant J in parentheses; signals of protons H-1, H-2, OCH_3 resonates at 4·08—4·10 ppm.

TABLE IV — *continued*

10 e	14	$C_{(7)}$-side chain
3·21 dd (19·5, 1·0)	2·43 s	4·32 d (6·1, 2 × H-1′); 5·06—5·41 mt (2 × H-3′); 6·03 ddd (17·1, 8·6, 6·1, H-2′)
3·00 dd (17·1, 1·2)	2·39 s	4·12 d (4·9, 2 × H-1′); 5·06—5·35 mt (2 × H-3′); 5·97 ddd (18·3, 9·8, 4·9, H-2′)
3·23 dd (19·5, 1·2)	2·43 s	3·82 t (6·1, 2 × H-1′); 4·86—5·27 mt (H-4′, 2 × H-5′)
2·97 dd (19·4, 1·0)	2·37 s	4·03 t (6·1, 2 × H-1′); 4·81—5·16 mt (H-4′, 2 × H-5′)
3·23 dd (19·5, 1·8)	2·41 s	4·30 dt (7·9, 6·1, H-1′); 5·10—5·51 mt (2 × H-3′); 5·87 mt (H-2′); 1·56 mt (2 × H-1″); 0·80 t (7·3, 3 × H-2″)
3·26 dd (19·5, 1·2)	2·43 s	4·15 tdd (7·3, 1·8, 1·2, H-1′); 5·03—5·35 mt (2 × H-3′), 5·92 mt (H-2′), 1·66 dq (7·3, 7·3, 2 × H-1″); 0·90 t (7·3, 3 × H-2″)
3·00 dd (18·0, 0·8)	2·41 s	3·92 dq (6·7, 6·7, H-1′); 5·03—6·06 mt (H-2′, 2 × H-3′); 1·72 mt (2 × H-1″); 0·75 t (7·3, 3 × H-2″)
3·02 dd (17·1. 1·2)	2·39 s	3·88 dt (6·7, 6·7, H-1′); 4·88—6·19 mt (H-2′, 2 × H-3′); 1·58 mt (2 × H-1″); 0·87 t (7·3, 3 × H-2″)
3·24 dd (18·9, 1·2)	2·43 s	3·87 t (6·1, 2 × H-1′); 2·31 mt (2 × H-2′); 4·92—6·14 mt (H-3′, 2 × H-4′)
3·00 dd (17·1, 1·2)	2·39 s	3·63 mt (2 × H-1′); 4·86—6·13 mt (H-3′, 2 × H-4′)
3·25 dd (18·6, 1·5)	2·43 s	4·26 dd (4·9, 1·4, 2 × H-1′); 5·69 mt (H-2′, H-3′); 1·71 dd (4·9, 1·5, 3 × H-4′)
2·98 dd (17·1, 1·2)	2·38 s	4·06 d (7·3, 2 × H-1′); 5·62 mt (H-2′, H-3′); 1·68 ddt (4·9, 1·5, 1·0, 3 × H-4′)
3·23 dd (18·9, 1·2)	2·44 s	4·45 dd (14·6, 1·5, H-1′b); 4·59 dd (14·6, 1·0, H-1′ a); 2·52 dd (1·5, 1·0, H-3′)
2·96 dd (18·9, 0·9)	2·40 s	4·28 dd (14·7, 1·2, H-1′ b); 4·42 dd (14·7, 1·2, H-1′ a); 2·35 t (1·2, H-3′)
3·00 dd (20·1, 1·2)	2·38 s	4·58 d (3·7, H-1′); 1·74 dsp (3·7, 6·7, H-2′); 0·88 d (6·7, 3 × H-3′); 0·93 d (6·7, 3 × H-4′)
3·17 dd (18·3, 1·8)	2·39 s	4·90 d (4·3, H-1′); 1·68 dsp (4·3, 6·4, H-2′); 0·77 d (6·4, 3 × H-3′); 0·88 d (6·4, 3 × H-4′)

and H-3 are practically identical to those of daunomycinone[7] throughout the whole series;

EXPERIMENTAL

Melting points were measured on Kofler hot stage apparatus. Optical rotation was measured by an automatic Bendix Ericsson polarimeter. Mass spectra were studied on a Varian MAT 311 spectrometer (energy of ionizing electrons 70 eV, ionizing current 1 mA, ion source temperature 200°C, direct inlet at 135–180°C). ^{1}H NMR spectra were recorded on a Jeol FX-60 instrument (FT mode, 59·797 MHz) at 25°C in deuteriochloroform. Tetramethylsilane was used as an internal standard. Chemical shifts (±0·02 ppm) are given in the δ-scale. Problems caused by signal overlap of the alicyclic ring and $C_{(7)}$—O— side chain protons were in most cases overcome by means of the partially relaxed spectra[6]. Signals were assigned by decoupling. ^{13}C NMR spectra were measured on the same spectrometer (15·036 MHz) with accuracy of ±0·06 ppm. Reported signal multiplicity is based on the off-resonance experiments. R_F values were determined by thin layer chromatography on DC-Fertigplatten (Kieselgel 60, Merck) in the system benzene–chloroform–ethyl acetate–methanol 7 : 7 : 3 : 1.

(7*S*)-9-Acetyl-7-O-allyl-4-methoxy-7,8,9,10-tetrahydro-6,9,11-trihydroxy-5,12-naphtacenequinone (*II*)

Daunomycinone (*I*, 170 mg) was dissolved in the mixture of benzene (6 ml) and xylene (6 ml). 2-Propen-1-ol (2 ml) and *p*-toluenesulfonic acid (50 mg) were added. The reaction was carried out 5 h at 120°C. Water was added and the products extracted with chloroform. Solvent was removed and the residue subjected to column chromatography on silica gel (according to Pitra); the eluent was benzene. Resulting mixture of compounds *II* and *III* was separated by preparative thin layer chromatography on Silufol 20 in the system benzene–chloroform–ethyl acetate–methanol 7 : 7 : 3 : 1.

Similarly were prepared compounds *IV*–*XVII*. In these cases two derivatives with configuration *S* and *R* at $C_{(7)}$ are formed. Exceptional are reactions with 2-methyl-2-propen-1-ol (products are two 7,9-ketals of daunomycinone, *IV* and *V*) and with 1-penten-3-ol (four products, *VIII* to *XI*). Diastereomers *VIII*, *IX* and *X*, *XI* were separated by thin layer chromatography on Silufol 20 n the system benzene–chloroform–methanol 10 : 2 : 0·1 (repeated development).

^{13}C NMR Spectra of Compounds *II*–*V*, *XVI* and *XVII*

II (C^2HCl_3): 25·0 q, 32·6 t, 33·9 t, 56·7 q, 68·7 d, 72·0 t, 75·5 s, 111·4 s (2 C), 118·0 t, 118·4 d, 119·7 d, 121·0 s, 134·1 d, 134·3 s, 135·0 s, 135·4 s, 135·5 d, 153·9 s, 156·5 s, 161·0 s, 186·7 s, 187·0 s, 212·7 s.

III (C^2HCl_3): 24·2 q, 31·6 t, 38·9 t, 56·7 q, 68·1 d, 71·0 t, 111·7 s (2 C), 117·1 t, 118·3 d, 119·7 d, 134·8 s, 135·5 d, 155·2 s, 156·3 s.

IV (C^2HCl_3): 16·0 q, 17·0 q, 24·7 q, 31·2 t, 31·6 t, 32·4 d, 56·7 q, 62·1 d, 77·5 s, 94·9 d, 111·5 s, 111·9 s, 118·5 d, 119·7 d, 121·1 s, 132·7 s, 135·4 s, 135·5 d, 137·4 s, 153·9 s, 155·4 s, 161·1 s, 186·9 s, 187·0 s, 210·1 s.

V (C^2HCl_3): 15·7 q, 17·0 q, 26·0 q, 32·4 t (2 C), 34·2 d, 56·8 q, 61·3 d, 77·8 s, 95·8 d, 109·3 s (2 C), 118·4 d, 119·7 d, 127·6 s, 135·7 d, 138·0 s, 154·3 s, 156·1 s, 162·9 s.

XVI (C^2HCl_3): 24·7 q, 33·4 t (2 C), 56·4 q, 58·6 t, 69·3 d, 75·1 s, 92·7 s, 111·1 s (2 C), 118·1 d. 119·6 d, 120·6 s, 133·3 s, 134·9 s, 135·4 d, 135·5 s, 155·6 s, 156·1 s, 160·8 s, 186·5 s, 186·7 s, 212·5 s.

XVII (C^2HCl_3 + hexadeuteriodimethyl sulfoxide): 23·5 q, 31·5 t, 37·6 t, 56·4 q, 57·8 t, 69·5 d, 74·2 s, 79·0 s, 112·4 s (2 C), 118·3 d, 119·3 d, 135·4 d, 154·0 s, 160·8 s, 186·2 s, 186·9 s.

Note: when some signal is not reported, its intensity was comparable with the noise.

REFERENCES

1. Arcamone F., Cassinelli G., Penco S. in the book: *Anthracycline Antibiotics* (H. S. El Khadem, Ed.), p. 59. Academic Press, New York 1962.
2. Fuchs E. F., Horton D., Weckerle W., Winter B.: J. Antibiot. *32*, 223 (1979).
3. Přikrylová V., Sedmera P., Jizba J. V., Vokoun J., Lipavská H., Podojil M., Vaněk Z.: This Journal *49*, 313 (1984).
4. Arcamone F., Franceschi G., Penco S., Selva A.: Tetrahedron Lett. *1969*, 1007.
5. Jizba J. V., Sedmera P., Vokoun J., Lipavská H., Podojil M., Vaněk Z.: This Journal *49*, 653 (1984).
6. Hall L. D., Preston C. M., Stevens J. D.: Carbohyd. Res. *41*, 41 (1975).
7. Arcamone F., Cassinelli G., Franceschi G., Mondelli R., Orezzi P., Penco S.: Gazz. Chim. Ital. *100*, 949 (1970).

Translated by the author (P. S.).