E-HOMOLUPANE DERIVATIVES SUBSTITUTED IN POSITION 17 AND 22a. ^{1}H NMR, ^{13}C NMR AND IR SPECTRA*

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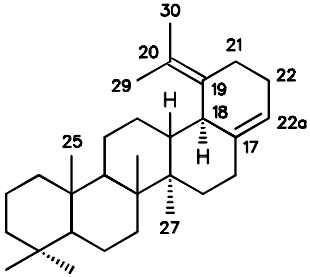
A series of derivatives with various oxygen functionalities in positions 17,22a or 19,20 was prepared from diene *I* and olefin *XVI* by addition and oxidation reactions. The structure of the obtained compounds was confirmed by ^{1}H NMR, ^{13}C NMR and IR spectroscopy. The kind of intramolecular association of the 17α-hydroxy group was studied in connection with modification of the side chain and substitution in position 22a. Complete assignment of the hydrogen signals and most of the coupling constants was accomplished using a combination of 1D and 2D NMR techniques. The ^{1}H and ^{13}C NMR spectra are discussed.

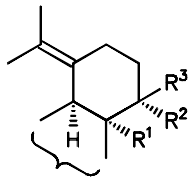
In connection with the preparation and confirmation of structure of the E-homolupane derivatives *I* and *XVI*, we described[1–4] some of their derivatives substituted in positions 17 and 22a. Now, we have extended this set by preparing further derivatives such as diols, their monoacetates and ketols with modified side chain. The obtained series of 17,22a-disubstituted derivatives with various functional groups in positions 19 or 19,20 was utilized for the study of interactions between these substituents.

Hydroxylation of diene *I* with osmium tetroxide affected only the 17(22a) double bond giving rise to diol *III*; the isopropylidene group in the side chain (unlike the isopropenyl group[5]) did not react (the ^{1}H NMR spectrum contained sp^2-methyl group signals at δ 1.735 and 1.692 and the ^{13}C NMR spectrum exhibited signals at δ 129.01 and 128.14 due to the sp^2-carbon atoms of the tetrasubstituted double bond). The diol *III* was characterized as the monoacetate *IV* (characteristic CH–OAc signals: δ 5.33 dd, 1 H and 2.09 s, 3 H) and its oxidation with chromium trioxide in pyridine gave ketol *V* (in the ^{1}H NMR spectrum the CH–OH signal of the starting diol *III* at δ 3.91 disappeared

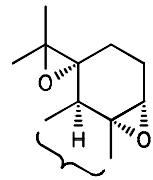
* Part CIV in the series Triterpenes; Part CIII: Collect. Czech. Chem. Commun. *59*, 1420 (1994).



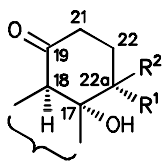
I



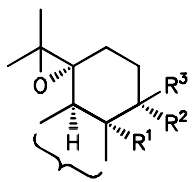
II, $R^1 = R^3 = H$; $R^2 = OH$
III, $R^1 = R^2 = OH$; $R^3 = H$
IV, $R^1 = OH$; $R^2 = OAc$; $R^3 = H$
V, $R^1 = OH$; $R^2 + R^3 = O$



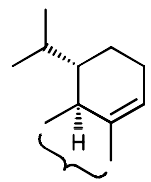
VI



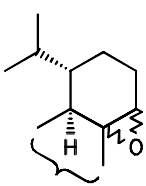
VII, $R^1 = OH$; $R^2 = H$
VIII, $R^1 = OAc$; $R^2 = H$
IX, $R^1 + R^2 = O$



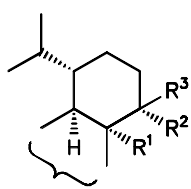
X, $R^1 = OH$; $R^2 = R^3 = H$
XI, $R^1 = R^3 = H$; $R^2 = OH$
XII, $R^1 = R^3 = H$; $R^2 = OAc$
XIII, $R^1 = R^2 = OH$; $R^3 = H$
XIV, $R^1 = OH$; $R^2 = OAc$; $R^3 = H$
XV, $R^1 = OH$; $R^2 + R^3 = O$



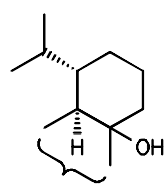
XVI



XVII



XVIII, $R^1 = OH$; $R^2 = R^3 = H$
XIX, $R^1 = R^3 = H$; $R^2 = OH$
XX, $R^1 = R^2 = OH$; $R^3 = H$
XXI, $R^1 = OH$; $R^2 = OAc$; $R^3 = H$
XXII, $R^1 = H$; $R^2 + R^3 = O$
XXIII, $R^1 = OH$; $R^2 + R^3 = O$



XXIV

Atoms in compounds *VII – IX* are numbered for the purpose of NMR only; the numbering does not correspond to the IUPAC nomenclature.

and the ^{13}C NMR spectrum exhibited a C=O signal at δ 209.88 instead of the CH–OH signal at δ 67.13 for *III*).

In contrast, epoxidation of diene *I* led to the diepoxide *VI*. The presence of the epoxy groupings was confirmed by IR absorption at 898 and 890 cm^{-1} and by the ^{13}C NMR spectrum (three C–O and one CH–O carbon signal at δ 64.54, 65.00, 60.36 and 57.27). As we have found already earlier[4], in addition reactions the 17(22a) double bond in diene *I* is attacked selectively from the α-side. The absence of hydrogen at C-17 in compounds *III* and *VI* did not alow a direct configurational proof using the vicinal interaction *J*(17,18); however, as a convincing argument served the observed long-range coupling between protons H-18 and H-21α (*J* ≈ 2 Hz for compounds *III* and *VI*): this can be explained only by *cis*-annelation of the rings D/E where the interacting protons are separated by four bonds in a planar zig-zag arrangement. For this reason we assigned configuration α to the functional groups introduced.

Ozonolysis of olefin *IV* afforded a trinorketone which was assigned structure *VIII* on the basis of the following observations. Its IR spectrum exhibited a band of carbonyl in a six-membered ring (1 716 cm^{-1}), bands of a hydroxyl (3 600 and 3 430 cm^{-1}) and a band of acetoxy group (1 728 cm^{-1}). The ^{13}C NMR spectrum indicated retention of the OH and OAc groups (carbon atoms of the type C–O and CH–O at δ 75.99 and 69.12), loss of three carbon atoms of the isopropylidene side chain, and the presence of a keto group (C=O at δ 212.64). A detailed analysis of signals due to E-ring protons confirmed unequivocally the presence of a keto group in position 19 as well as retention of the *cis*-annelation D/E (*J*(18,21α) = 1.5 Hz). As a side-product of the ozonolysis we isolated an epoxy derivative which was assigned the structure *XIV*. Its IR spectrum showed the presence of a hydroxy group (3 540 cm^{-1}), an acetoxy group (1 729 cm^{-1}) and an epoxy group (860 cm^{-1}). The ^{13}C NMR spectrum proved retention of the oxygen substituents in positions 17 and 22a (δ 74.95 and 69.63) and epoxidation of the isopropylidene double bond (instead of sp^2-carbon signals the spectrum exhibited signals of C–O carbon atoms at δ 68.01 and 63.27). Hydrolysis of monoacetates *VIII* and *XIV* afforded diols *VII* and *XIII* which were oxidized to ketols *IX* and *XV*.

Lithium aluminium hydride reduction of diepoxide *VI* took place only in the position 17,22a, the other epoxy group in the side chain remaining intact[3]. The IR spectrum of the obtained epoxy alcohol *X* exhibited bands of an epoxy group (908 and 888 cm^{-1}) and a hydroxyl (3 430 cm^{-1}). The resistance of the hydroxyl toward oxidation and acetylation indicated its tertiary character. This was confirmed by the absence of signals of CH–O grouping in the proton as well as carbon NMR spectra and by the presence of three quaternary carbon atoms of the type C–O in the ^{13}C NMR spectrum (δ 63.37, 69.36 and 74.37) of which the first two belonged to the epoxide group and the third to the C–OH grouping in position 17. The configuration of the 17-hydroxy group was confirmed by the coupling constant *J*(18,21α) = 2.6 Hz. Epoxy alcohol *XI* was

prepared by epoxidation of the known[4] unsaturated alcohol *II* and characterized as acetate *XII*.

Because of an easier access of the attacking reagent to the 19(20)-double bond from the α-side (as evident from models), the epoxy groups in the side chain were assigned the α-configuration. This was confirmed by formation of an intramolecular hydrogen bond between the 17α-hydroxyl and the 19,20-epoxy group in the compounds *X*, *XIII – XV* and by further arguments following from the NMR spectra (see Discussion).

Epoxidation of olefin *XVI* afforded an unseparable mixture of α- and β-epoxides *XVII*. Moreover, we found that the epoxides rearranged during the chromatography because in an attempted separation we isolated also the ketone *XXII* (prepared in ref.[1]). The same rearrangement of an analogous epoxide was observed by us previously[2]. The α : β isomer ratio (8 : 9) follows from the ratio of alcohols *XVIII* and *XXIV* isolated on reduction of the mixture of isomeric epoxides *XVII* with lithium aluminium hydride. The structure of both the alcohols was derived from ^{1}H NMR spectra: the 17α-hydroxy group effects a significant downfield shift of the 20-H signal, accompanied by a smaller downfield shift of both methyl groups in the isopropyl substituent (see Table I), which is not possible for the 17β-hydroxyl. Compound *XIX* was described in ref.[1], compounds *XX*, *XXI* and *XXIII* in ref.[2].

DISCUSSION

NMR Spectra

Complete structural assignment of the proton signals in triterpenes represents a difficult task even for spectra taken at high frequencies (500 MHz) because of a multitude of spin–spin interactions and overlapping of multiplets which, moreover, may have a higher order character. So far, the available pertinent data are only very sporadical and usually incomplete (see e.g. ref.[6]). To achieve the goal, it is necessary to combine various 1D and 2D NMR techniques and this approach has been used also in the present study. In the 1D NMR spectra (500 MHz) of the studied triterpenes *III – VII*, *IX – XIII*, *XV* and *XXII* only the intense methyl signals were identifiable and several signals of protons on rings D and E in the neighbourhood of oxygen substituents or double bonds appeared at lower field (δ > 2.00). Signals of interacting protons were assigned using 2D-COSY spectra that identified individual spin systems, isolated by carbon atoms C(4), C(8), C(10) and C(14) (and, according to the substitution type, also by C(17) and C(19)). In most of the compounds studied (*III – VII*, *IX*, *X*, *XIII* and *XV*) , the alicyclic protons form thus five spin systems *S1 – S5* (see e.g. ketol *V* in Fig. 1) whereas in the remaining compounds (*XI*, *XII* and *XXII*) their number is reduced to three by interconnecting the spin systems *S3*, *S4* and *S5*. The structural identification of the individual spin systems followed from the number of protons, signals unequivocally assignable according to the chemical shift and multiplicity (e.g. CH–O), characteristic long-range

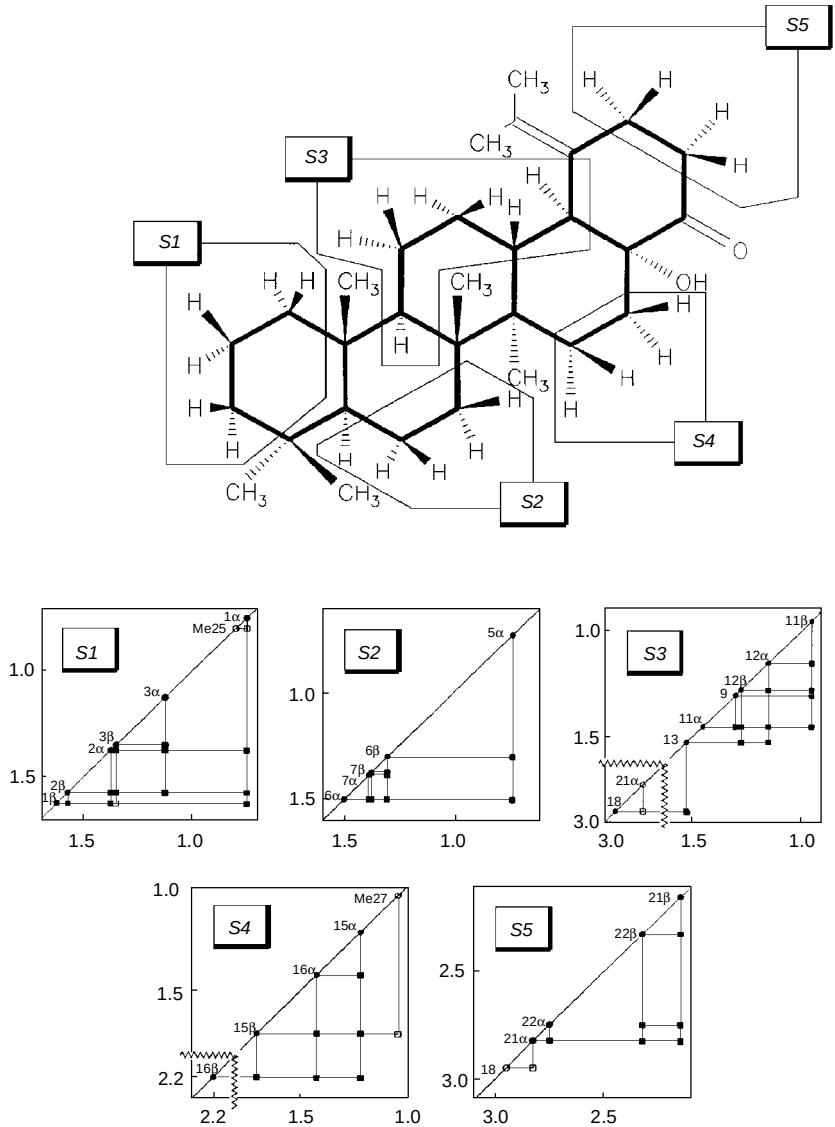


FIG. 1

Spin systems (*S1* to *S5*) of protons in compound *V* and schematic diagrams of the corresponding 2D-COSY subspectra: ● diagonal peaks of protons of the given spin system, ❍ diagonal peaks of another proton connected to the given spin system via long-range coupling, ■ cross-peaks corresponding to geminal and vicinal couplings, ❒ cross-peaks corresponding to long-range couplings

TABLE I
^{1}H NMR chemical shifts (in ppm) of selected protons in compounds *III* – *XV*, *XVIII*, *XXII* and *XXIV*[a]

Proton	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI*	*XII*	*XIII*	*XIV*	*XV*	*XVIII*	*XXII*	*XXIV*
H-13	1.79	1.85	1.51	1.77	1.95	[b]	1.71	1.77	1.78	1.83	1.75	[b]	1.42	[b]	1.29[c]	[b]
H-15α	1.22[c]	1.15	1.22	1.15	1.27	[b]	1.27	1.18	1.05	0.99	1.19	[b]	1.20	[b]	1.03	[b]
H-15β	1.65	1.64	1.70	1.63	1.72	[b]	1.72	1.65[c]	1.71	1.71	1.65	[b]	1.67	[b]	1.64[c]	[b]
H-16α	1.42	1.52	1.42	2.07	1.37[c]	[b]	1.41	1.32[c]	1.49	1.44[c]	1.38	[b]	1.38	[b]	1.34[c]	[b]
H-16β	2.14	1.73	2.20	1.42[c]	2.11	[b]	2.18	1.55[c]	1.96	1.57	2.12	[b]	2.19	[b]	2.11	[b]
H-17	–	–	–	–	–	–	–	–	1.71[c]	1.96	–	–	–	–	2.51	–
H-18	2.70	2.70	2.95	1.90	2.28	2.31	2.55	1.54	1.60[c]	1.64	1.71	[b]	1.90	[b]	1.99	[b]
H-20α	–	–	–	–	–	–	–	–	–	–	–	–	–	2.25	1.85	[b]
H-21α	2.51	2.57	2.83	1.26[c]	2.26	[b]	2.67[d]	1.32[c]	1.44	1.43[c]	1.45	[b]	1.80	[b]	1.81	[b]
H-21β	1.79	1.86	2.14	1.70	2.50	2.52	2.72[d]	[a]	1.78	1.81	1.81	[b]	2.17	[b]	1.75	[b]
H-22α	1.28[c]	1.57[c]	2.74	2.19	2.03	[b]	3.18[d]	1.94	1.55[c]	1.60[c]	1.74[c]	[b]	3.16	[b]	2.29	[b]
H-22β	1.97	1.86[c]	2.31	2.09	2.14	[b]	2.62[d]	1.70[c]	2.07	2.05	2.00	[b]	2.35	[b]	2.15	[b]
H-22a	3.91	5.33	–	2.96	4.25	5.55	–	1.97	4.01	5.27	3.90	5.35	–	[b]	–	[b]
H-23	0.852	0.846	0.846	0.861	0.848	0.843	0.844	0.853	0.851	0.845	0.853	0.850	0.848	0.837	0.839	0.837
H-24	0.796	0.796	0.787	0.804	0.796	0.797	0.789	0.800	0.799	0.798	0.799	0.801	0.790	0.790	0.786	0.789
H-25	0.800	0.833	0.811	0.866	0.839	0.843	0.819	0.855	0.851	0.850	0.850	0.850	0.828	0.837	0.814	0.837
H-26	1.003	1.038	0.898	1.022	1.045	1.077	0.974	1.036	1.044	1.080	1.023	1.070	0.913	0.979	0.892	1.035
H-27	1.062	1.053	1.038	1.039	0.990	0.981	0.930	0.992	0.950	0.933	1.011	0.999	0.987	0.979	0.938	0.954
H-29	1.735	1.741	1.830	1.254	–	–	–	1.302	1.300	1.302	1.313	1.320	1.392	0.907	0.973	0.863
H-30	1.692	1.697	1.789	1.238	–	–	–	1.289	1.285	1.289	1.307	1.306	1.392	0.849	0.969	0.803
OAc	–	2.09	–	–	–	2.12	–	–	–	2.06	–	2.12	–	–	–	–

[a] Typical chemical shift values of A, B and C ring protons (derived for compound *V*) are: H-1α 0.75; H-1β 1.62; H-2α 1.37; H-2β 1.58; H-3α 1.12; H-3β 1.35; H-5 0.72; H-6α 1.50; H-6β 1.30; H-7α ≈1.38; H-7β ≈1.38; H-9 ≈1.30; H-11α 1.46; H-11β 0.96; H-12α 1.15; H-12β 1.28. [b] The parameter value could not be determined (1D NMR spectra at 100 MHz and/or 200 MHz were measured only). [c] The position of signals was derived from 2D-COSY spectrum only. [d] The parameter values were obtained from simulation-iteration analysis of four-spin system of protons in positions 21 and 22.

TABLE II

Coupling constants (J in Hz) of selected protons in compounds *III* – *XV* and *XXII*[a]

Protons	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI*	*XII*	*XIII*	*XIV*	*XV*	*XXII*
13,18	12.0	12.0	12.1	11.4	12.3	12.8	12.5	12.0	12.5	12.4	≈11.5	[b]	12.0	11.5
15α,15β	≈14	13.5	13.6	13.2	13.8	[b]	13.8	13.0	13.4	13.7	13.2	[b]	13.7	13.4
15α,16α	4.1	4.0	4.6	4.5	4.3	[b]	4.7	4.3	4.2	4.0	4.5	[b]	4.6	4.5
15α,16β	3.1	3.1	2.9	2.8	3.1	[b]	2.8	2.2	2.6	3.0	2.9	[b]	2.8	3.0
15β,16α	≈14	13.5	13.6	13.5	13.8	[b]	13.4	[b]	≈13	13.7	≈13.5	[b]	13.7	[b]
15β,16β	4.1	3.8	4.4	4.5	4.1	[b]	4.3	[b]	4.1	4.3	4.2	[b]	4.4	4.4
16α,16β	13.2	13.2	13.0	13.5	13.3	[b]	12.8	[b]	14.1	13.8	13.7	[b]	13.3	13.6
16α,17	–	–	–	–	–	–	–	–	≈4.5	4.4	–	–	–	5.0
16β,17	–	–	–	–	–	–	–	–	2.6	2.1	–	–	–	2.2
17,18	–	–	–	–	–	–	–	–	[b]	4.4	–	–	–	5.6
18,21α	1.8	1.4	2.0	<2	1.8	≈1.5	1.9	2.6	2.0	1.8	1.7	[b]	2.4	1.2
21α,21β	14.0	13.4	14.0	14.2	14.3	≈14	15.9[c]	[b]	13.6	13.9	13.6	[b]	14.0	13.8
21α,22α	4.5	4.5	7.2	8.6	4.8	[b]	7.8[c]	4.3[d]	4.1	[b]	4.3	[b]	7.2	5.9
21α,22β	2.8	2.5	1.9	[b]	2.5	[b]	4.3[c]	[b]	3.1	2.8	2.7	[b]	1.8	5.2
21β,22α	[b]	[b]	13.4	10.7	14.3	≈12	10.8[c]	13.5[d]	13.6	13.9	13.6	[b]	13.8	10.5
21β,22β	5.4	[b]	5.4	8.8	6.6	≈8.5	7.8[c]	[b]	4.1	4.0	3.8	[b]	5.3	5.2
22α,22β	12.4	[b]	14.6	15.7	14.4	[b]	15.8[c]	13.5[d]	11.7	12.0	≈12	[b]	15.0	16.3
22α,22a	11.0	12.0	–	≈0	11.0	10.1	–	13.5[d]	10.9	11.3	11.0	11.5	–	–
22β,22a	4.5	4.9	–	4.5	4.5	6.5	–	4.5[d]	4.9	5.0	5.0	5.3	–	–
25,1α	1.0	≈1	0.8	[b]	1.0	[b]	1.0	1.0	[b]	0.8	1.0	[b]	0.9	1.0
27,15β	0.8	[b]	0.9	[b]	0.7	[b]	0.6	0.5	[b]	0.6	0.7	[b]	[b]	0.8

[a] Typical coupling constants of A, B and C ring protons (derived for compound *V*) are: $J(1\alpha,1\beta) = 13$; $J(1\alpha,2\alpha) = 4.1$; $J(1\alpha,2\beta) = 13$; $J(1\beta,2\alpha) = 3.3$; $J(1\beta,2\beta) = 3.3$; $J(1\beta,3\beta) = 1.5$; $J(2\alpha,2\beta) = 13$; $J(2\alpha,3\alpha) = 4.1$; $J(2\alpha,3\beta) = 3.3$; $J(2\beta,3\alpha) = 13.8$; $J(2\beta,3\beta) = 3.7$; $J(3\alpha,3\beta) = 13.8$; $J(5,6\alpha) = 2.4$; $J(5,6\beta) = 12.0$; $J(6\alpha,6\beta) = 12.6$; $J(6\alpha7\alpha) \approx 3.3$; $J(6\alpha,7\beta) \approx 3.3$; $J(6\beta,7\alpha) = 12$; $J(6\beta,7\beta) = 4.4$; $J(7\alpha,7\beta) = 13$; $J(9,11\alpha) = 3.2$; $J(9,11\beta) = 12.7$; $J(11\alpha,11\beta) = 13$; $J(11\alpha,12\alpha) = 4.6$; $J(11\alpha,12\beta) = 3$; $J(11\beta,12\alpha) = 13$; $J(11\beta,12\beta) = 4.5$; $J(12\alpha,12\beta) = 13$; $J(12\alpha,13) = 12.6$; $J(12\beta,13) = 3.7$; additional coupling constants: in *III* – *V*: $J(29,21\beta) \approx 1.2$ and $J(30,21\beta) \approx 1.7$; in *X*: $J(22a\alpha,22\alpha) = 4.3$ and $J(22a\alpha,22a\beta) = 14.0$; in *XI* and *XII*: $J(17,22a) \approx 11$; in *XXII*: $J(18,19) = 2.8$, $J(19,20) = 8.3$, $J(20,29) = J(20,30) = 6.5$, $J(17,22\alpha) = 0.8$, $J(19,21\alpha) \approx 5.5$ and $J(19,21\beta) \approx 4.5$. [b] The parameter value could not be determined. [c] The parameter values were obtained from simulation-iteration analysis of four-spin system of protons in positions 21,22. [d] *J*-Values derived from the spectrum of TAC-derivative of *X*.

TABLE III
Carbon-13 chemical shifts (in ppm) of compounds *III* – *XV* and *XXII*

Carbon	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI*	*XII*	*XIII*	*XIV*	*XV*	*XXII*
C-1	40.40	40.38	40.38	40.44	40.34	40.36	40.30	40.44	40.38	40.41	40.43	40.47	40.43	40.31
C-2	18.68	18.67	18.66	18.64	18.59	18.60	18.57	18.67	18.67	18.68	18.65	18.69	18.65	18.68
C-3	42.07	42.08	42.04	41.97	41.98	42.03	41.95	42.03	42.04	42.08	42.01	42.06	42.01	42.08
C-4	33.27	33.27	33.25	33.24	33.27	33.26	33.24	33.27	33.27	33.27	33.26	33.34	33.25	33.24
C-5	56.52	56.51	56.44	56.38	56.43	56.45	56.34	56.43	56.43	56.45	56.43	56.47	56.39	56.38
C-6	18.55	18.54	18.51	18.47	18.51	18.52	18.46	18.51	18.52	18.52	18.47	18.50	18.45	18.57
C-7	33.96	33.88	34.00	34.32	34.02	33.98	34.05	34.07	33.92	33.84	34.00	33.95	34.04	33.88
C-8	41.13	41.14	41.09	41.23	41.00	41.13	41.05	41.33	41.28	41.24	41.16	41.17	41.07	41.65
C-9	50.80	50.78	50.55	50.76	50.56	50.54	50.28	50.75	50.77	50.75	50.74	50.75	50.59	50.22
C-10	37.47	37.45	37.42	37.44	37.60	37.49	37.42	37.45	37.47	37.47	37.44	34.47	37.42	37.40
C-11	21.05	21.01	20.82	21.16	20.72	20.66	20.48	21.20	21.18	21.13	21.12	21.12	20.90	20.79
C-12	25.36	25.26	25.33	26.20	26.26	26.09	26.12	25.61	25.60	25.65	25.61	25.66	25.50	24.71
C-13	36.79	37.05	37.29	40.80	38.01	37.88	38.14	37.58	35.54	35.39	37.10	37.36	38.08	38.88
C-14	41.18	41.11	40.87	40.90	40.71	40.79	40.60	41.10	41.44	41.41	41.09	41.20	40.90	40.96
C-15	27.51	27.45	28.22	30.60	27.85	27.71	28.44	27.97	25.50	25.54	27.45	27.32	28.08	26.76
C-16	29.10	30.20	28.56	19.38	30.95	31.16	29.50	35.50	21.67	21.92	28.32	30.16	28.78	21.82

TABLE III
(*Continued*)

Carbon	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI*	*XII*	*XIII*	*XIV*	*XV*	*XXII*
C-17	74.72	73.60	≈77.0[a]	60.36	≈77.0[a]	75.99	78.23	74.37	41.24	38.61	76.01	74.95	78.27	45.47
C-18	47.83	48.00	49.35	41.11	61.10	60.64	61.20	45.58	41.96	41.25	45.70	46.69	47.00	40.67
C-19	129.01	128.77	131.23	64.54	212.64	211.39	209.70	69.36	68.12	67.73	68.58	68.01	67.56	39.99
C-20	128.14	127.63	126.40	65.00	–	–	–	63.37	65.29	65.31	63.51	63.27	63.65	28.32
C-21	23.55	23.45	24.58	21.46	36.65	36.23	36.14	24.24	24.54	24.22	24.25	24.15	26.02	20.45
C-22	31.84	27.45	37.55	30.72	29.72	25.77	35.01	18.87	32.78	28.71	29.44	24.54	34.11	37.68
C-22a	67.13	70.56	209.88	57.27	66.33	69.12	206.73	30.72	66.04	68.96	66.46	69.63	208.57	213.84
C-23	33.35	33.34	33.35	33.30	33.32	33.31	33.31	33.33	33.33	33.34	33.32	33.28	33.33	33.35
C-24	21.53	21.52	21.53	21.52	21.50	21.51	21.50	21.53	21.53	21.53	21.50	21.53	21.52	21.53
C-25	16.27	16.24	16.20	16.44	16.27	16.22	16.17	16.37	16.34	16.30	16.34	16.32	16.30	16.15
C-26	15.82	15.86	15.73	16.15	15.77	15.82	15.66	16.00	16.00	16.04	15.92	15.98	15.85	15.71
C-27	14.80	14.87	14.35	14.36	14.44	14.46	14.01	14.55	14.31	14.32	14.70	14.79	14.36	14.08
C-29[b]	20.62	20.73	20.91	22.23	–	–	–	21.71	22.11	22.06	21.87	21.98	21.99	21.12
C-30[b]	20.62	20.65	20.73	20.48	–	–	–	20.34	20.83	20.83	20.52	20.50	20.62	20.35
OAc	–	170.74	–	–	–	170.15	–	–	–	171.06	–	171.08	–	–
		21.25				21.01				21.19		21.27		

[a] Overlapped with the strong signal of solvent. [b] The methyl signals may be interchanged.

couplings either with methyl signals (e.g. $J(1\alpha,25)$, $J(15\beta,27)$ or $J(21\beta,29)$ and $J(21\beta,30)$ in derivatives with 19(20) double bond) or between protons of the same ($J(1\beta,3\beta)$ in *S1*) or neighbouring spin systems ($J(18,21\alpha)$ between *S3* and *S5*). The proton multiplets of the individual spin systems were then analyzed in the 1D and 2D-*J*-resolved spectra which enabled their structural assignment and mostly also determination of the coupling constants. Even in spite of significant overlap of signals in the range δ 1 – 2, the appearance of strongly interacting systems in the analyzed spectra was only sparce (mostly protons H-7α and H-7β). The chemical shifts and coupling constants of the protons are summarized in Tables I and II. Since only the ring E was structurally modified, the chemical shifts and coupling constants of farther protons on rings A – C were almost identical. The *cis*-annelation of rings D and E in compounds *XI*, *XII* and *XXII* followed from the small value of $J(17,18)$ (about 5 Hz) and in the 17-substituted derivatives from the observed long-range coupling constants $J(18,21\alpha)$ in the region 1.2 – 2.6 Hz. The vicinal coupling constants for the E-ring protons were generally in accord with the chair conformation. The signals of the 23-, 24- and 25-methyl groups on the ring A were only little sensitive to substitution on the ring E and their shifts corresponded to the values described for other triterpenic "3-deoxy" derivatives (see ref.[7] and references therein), including the characteristic fine splitting of the 25-methyl signal. The 26- and 27-methyl signals were located downfield, the 27-methyl signal usually being broadened or split by long-range interaction with the H-15β proton. In the isopropyl group, the 29- and 30-methyl signals appeared as characteristic doublets (J = 6.5 Hz), in the isopropylidene group, these signals showed homoallylic coupling with the proton H-21β ($J \approx$ 1.7 and 1.2 Hz). According to a difference 1D NOE spectrum, the lowfield signals with a somewhat smaller coupling constant belonged to the *exo*-methyl group (*cis* relative to C-21). The α-configuration of the 19,20-epoxy group and the structural assignment of the 29- and 30-methyl groups in the epoxy derivatives was proven using 2D-ROESY spectrum of the epoxy acetate *XII*. Whereas the lowfield methyl at δ 1.302 showed ROESY peaks with the H-21α and H-21β protons (and thus the *syn*-orientation relative to C-21), the upfield methyl at δ 1.289 afforded ROESY peaks with the protons H-12α, H-12β and H-18. This is in accord with the α-configuration of the 19,20-epoxide for which models show close proximity of the methyl groups with the protons mentioned (2.6 to 3.1 Å). Protons of the tertiary as well as secondary OH groups, if detectable at all, appeared as singlets and gave thus no information on their orientation or intramolecular hydrogen bonds.

The carbon signals in ^{13}C NMR spectra of *III* – *XV* and *XXII* (Table III) were assigned on the basis of the carbon atom type (CH_3, CH_2, CH or C distinguished by "attached proton test" spectra[8]), characteristic chemical shifts, substituent effects and comparison with literature data (see ref.[9] and references therein). Substitution of the ring E had only very small effect on the chemical shifts of carbon atoms in the rings A – C.

TABLE IV

TAI-acylation shifts of selected protons and carbon atoms in hydroxy compounds *III – V, VII, IX – XI* and *XV*

Parameter	17α-OH derivatives					22aα-OH derivative	17α,22aα-diOH derivatives		
	IV	*V*	*XV*	*X*	*IX*	*XI*	*III*	*XIII*	*VII*
Proton									
H-13	0.07	0.04	0.00	0.08	0.10	0.03	0.11	0.11	0.12
H-15α	0.09	0.04	0.07	0.10	0.05	0.00	0.08	0.09	0.11
H-15β	0.04	0.29	0.17	[a]	0.14	0.04	0.10	0.12	0.12
H-16α	1.21	0.41	0.88	1.43	0.68	0.01	1.35	1.33	0.56
H-16β	0.02	0.31	0.05	[a]	0.53	–0.36	–0.32	–0.39	0.55
H-17	–	–	–	–	–	0.32	–	–	–
H-18	1.21	0.58	1.11	1.29	0.31	0.08	1.23	1.32	1.10
H-21α	0.01	0.06	–0.05	[a]	0.03	0.04	0.12	–0.06	0.15
H-21β	0.05	–0.02	–0.01	[a]	–0.06	0.07	0.13	0.13	0.14
H-22α	0.27	–0.10	–0.01	[a]	–0.18	0.15	0.62	0.52	0.26
H-22β	–0.09	0.08	0.10	[a]	0.08	0.11	–0.03	0.02	0.29
H-22a	0.19	–	–	[a]	–	1.35	1.65	1.68	1.55
H-26	0.00	0.02	0.01	0.00	0.00	0.04	0.05	0.05	0.06
H-27	0.11	0.04	0.07	0.10	0.06	0.00	0.11	0.09	0.11
H-29[b]	–0.09	–0.04	–0.08	–0.06	–	0.02	–0.07	–0.05	–
H-30[b]	–0.08	–0.06	–0.08	–0.07	–	0.01	–0.06	–0.08	–
Carbon									
C-13	1.22	–0.40	0.33	0.81	–0.73	–0.12	1.48	1.32	[c]
C-14	–0.11	–0.09	0.03	–0.13	0.07	–0.06	0.06	–0.09	[c]
C-15	0.58	0.31	0.32	0.46	–0.12	–0.03	0.63	0.48	[c]
C-16	–5.78	–2.55	–4.02	–4.87	–3.69	0.18	–4.57	–4.10	[c]
C-17	17.43	12.61	10.87	15.92	10.07	–2.68	15.79	12.96	[c]
C-18	–6.44	–2.70	–4.78	–6.22	–1.09	–0.68	–6.02	–6.23	[c]
C-19	–2.61	–1.18	–2.88	–1.96	–2.19	–0.58	–3.52	–3.37	[c]
C-20	0.97	–1.40	–1.52	–0.67	–	0.34	0.98	–0.59	[c]
C-21	–0.31	1.41	0.84	0.02	1.29	–0.43	–0.61	0.09	[c]
C-22	–0.25	1.36	1.16	–0.16	0.69	–4.20	–4.77	–4.60	[c]
C-22a	–1.41	–4.44	–4.72	–1.52	–5.03	7.27	5.82	5.20	[c]
C-26	0.05	0.05	0.10	0.08	0.00	0.00	0.09	0.09	[c]
C-27	0.00	–0.05	–0.07	0.05	–0.07	0.00	0.06	0.04	[c]
C-29[b]	–0.14	–0.04	0.06	0.03	–	–0.10	–0.03	–0.03	[c]
C-30[b]	–0.14	0.02	–0.13	–0.31	–	–0.03	–0.06	–0.28	[c]

[a] The parameter value could not be determined. [b] The values may be interchanged. [c] The carbon-13 NMR spectrum of TAC-derivative was not obtained due to very poor solubility.

The presence of OH groups in the hydroxy derivatives was proven by in situ acylation with trichloroacetyl isocyanate (TAI-method; see refs[10,11]), followed by ^{1}H and ^{13}C NMR spectroscopy. The observed TAI-acylation shifts are given in Table IV. The spectra of compounds with tertiary OH group (*IV*, *V*, *IX*, *X* and *XV*) showed significant downfield TAI-acylation shifts of protons in positions β (16α, 16β, 18 or 22a) and their values reflected the effect of substitution in the position 22a. Moreover, the derivatives with secondary OH group (alcohol *XI* and diols *III*, *VII* and *XIII*) exhibited characteristic acylation shifts in the position α (1.35 ppm for *XI*, 1.55 – 1.68 ppm for *III*, *VII* and *XIII*) and smaller downfield shifts of protons in the position β (H-22α, H-22β and,

TABLE V
Wavenumbers (ν_{max}, cm^{-1}), halfbandwidths ($\Delta\nu_{1/2}$, cm^{-1}) and relative intensities ($\varepsilon_{rel} = 100\varepsilon_i/\Sigma\varepsilon_i$) of O–H stretching vibration in hydroxy derivatives *II – V*, *VII – XI*, *XIII – XV*, *XVIII – XXI* and *XXIII*

Compound	Free OH			Associated OH								
							17 – 22a			17 – 19,20		
	ν_{max}	$\Delta\nu_{1/2}$	ε_{rel}	ν_{max}	$\Delta\nu_{1/2}$	ε_{rel}	ν_{max}	$\Delta\nu_{1/2}$	ε_{rel}	ν_{max}	$\Delta\nu_{1/2}$	ε_{rel}
II	3 626	21	65	–	–	–	–	–	–	–	–	–
III	3 626	26	11	–	–	–	3 571	28	46	3 556	26	43
IV	–	–	–	–	–	–	3 596	15	74	3 565	26	26
V	–	–	–	–	–	–	3 589	17	51	3 547	30	49
VII	3 627	20	13	3 612	17	34	3 577	22	37	3 532[a]	25	16
VIII	–	–	–	3 606[b]	16	20	3 596	12	80	–	–	–
IX	–	–	–	–	–	–	3 589[c]	18	100	–	–	–
X	–	–	–	–	–	–	–	–	–	3 549	37	100
XI	3 625	22	45	3 600	16	55	–	–	–	–	–	–
XIII	–	–	–	–	–	–	3 551	28	43	3 536	34	57
XIV	–	–	–	–	–	–	–	–	–	3 541	40	100
XV	–	–	–	–	–	–	–	–	–	3 519	41	100
XVIII	3 628[b]	14	13	3 605	25	87	–	–	–	–	–	–
XIX	3 625	22	70	3 603	21	30	–	–	–	–	–	–
XX	3 630	15	27	3 620	22	29	3 575	35	44	–	–	–
XXI	–	–	–	–	–	–	3 596	14	100	–	–	–
XXIII	–	–	–	–	–	–	3 585	18	100	–	–	–

[a] Band due to self-association. [b] Shoulder. [c] Asymmetric band.

in addition, H-17 in alcohol *XI*). The ^{13}C NMR spectra showed characteristic differences between tertiary and secondary alcohols in the TAI-acylation shifts for the α-position (10 – 17.5 ppm at C-17 vs 5.2 – 7.3 ppm at C-22a) and smaller upfield shifts for the neighbouring β-positions (−1.4 to −6.4 ppm), in accord with the literature[12].

IR Spectra

The IR spectroscopy was used for the study of intramolecular association of the 17α-hydroxy group which can form a hydrogen bond with an acceptor in the side chain as well as with a neighbouring group in position 22a, depending on the modification of the side chain and substitution in the position 22a. Parameters of the observed bands, ν(OH), are given in Table V. The following conclusions can be made.

The 22aα-monohydroxy derivatives *II*, *XI* and *XIX* exhibited only a free hydroxyl band, irrespective of the type of the side chain, because the distance of the OH group from the potential acceptor is too great. Naturally, also the 17α-hydroxy derivative *XVIII* with the isopropyl side chain, unsubstituted in position 22a, had only a free hydroxyl band. The bands had a distinguished doublet structure due to rotation isomerism of the OH group[13,14]. In diol *XX*, monoacetate *XXI* and ketol *XXIII* with the isopropyl side chain, the 17α-hydroxyl formed an intramolecular hydrogen bond with the 22a-substituent. Judging from the weak hydrogen bond and mutual orientation of the 17α-hydroxy and 22a-keto groups, we assume that in ketols *V*, *IX* and *XXIII* the 17α-hydroxyl is associated with the keto group by means of its π-orbital (see refs[15,16]). In the monoacetates *IV*, *VIII* and *XXI*, the hydroxyl associates with the electron pair of the alkoxy group (ref.[17]).

The 17α-hydroxy derivatives *III*, *IV* and *V*, containing the 19(20) double bond, exist in solution as an equilibrium mixture of two forms with intramolecular hydrogen bond involving either the double bond or the neighbouring 22a-substituent, the latter being weaker (smaller Δν(OH)). In the spectrum of diol *III*, the 17α-hydroxyl bands of both the hydrogen-bonded forms overlapped and also a small amount of the conformer with nonassociated 22aα-OH group was present. The 19-oxo group does not participate in the association and thus in compounds *VII – IX* the 17α-OH group forms hydrogen bond only with substituents in position 22a. The parameters of the ν(OH) bands for 19-oxo, 19-isopropyl and 19-isopropylidene derivatives were practically identical (see Table V).

When an α-epoxy group is present in position 19,20 then, because of its basicity and good steric accessibility, the 17α-OH group in compounds *X*, *XIII – XV* forms a hydrogen bond only to the epoxy group, irrespective of the substituent in position 22a. In diol *XIII* the band due to 17α-hydroxy group associated with the epoxy group overlapped with that of 22aα-hydroxyl associated with the 17α hydroxyl. The presence of intramolecular hydrogen bond to the 19,20 α-epoxy group in compounds *X*, *XIII – XV* confirms the *cis*-configuration of the oxygen groups in positions 17 and 19.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Optical rotation was measured in chloroform on an automatic polarimeter ETL-NPL (Bendix-Ericsson) with an accuracy ±2°. Infrared spectra were recorded in chloroform (unless stated otherwise) on UR-20 (Zeiss, Jena) and PE 684 (Perkin–Elmer) spectrometers, wavenumbers are given in cm^{-1}. Hydroxyl stretching vibrations were measured in tetrachloromethane at concentrations lower than $5 . 10^{-3}$ mol l^{-1} on a PE 684 instrument equipped with a datastation and their parameters were obtained by mathematical separation using the Cauchy profile function (accuracy minimum 1 cm^{-1} for ν_{max} and 2 cm^{-1} for $\Delta\nu_{1/2}$). Proton and ^{13}C NMR spectra were measured on FT NMR spectrometers Varian XL-200 (^1H at 200 MHz and ^{13}C at 50.3 MHz) or Varian UNITY-500 (^1H at 500 MHz and ^{13}C at 125.7 MHz) in deuteriochloroform with tetramethylsilane as internal standard (for the ^{13}C NMR data δ ($CDCl_3$) = 77.0 ppm). For the previously prepared compounds *XVIII* and *XXIV* only the ^1H NMR spectra were measured on a CW spectrometer Varian HA-100 (at 100 MHz). Optical rotatory dispersion was measured on a JASCO-ORD/UV-5 instrument in dioxane, CD spectra were taken on a Roussel–Jouan 185 spectrometer, also in dioxane. Column chromatography was performed on silica gel (Silpearl, Kavalier, Votice) or neutral alumina. Preparative thin-layer chromatography was carried out on Merck 60G silica gel. Spots were detected by UV light at 254 nm after spraying with 0.2% morin solution in methanol. Purity of the samples was checked by thin-layer chromatography on Silufol (Kavalier, The Czech Republic), detection with 10% ethanolic solution of phosphomolybdic acid. Analytical samples were dried over phosphorus pentoxide under diminished pressure at 100 °C for 10 h. The "usual work-up" means the following procedure: the reaction mixture was diluted with water, the product was taken up in ether, the ethereal extract was repeatedly washed with water and then in succession with dilute (1 : 4) hydrochloric acid, water, 5% sodium carbonate and water. Solutions in organic solvents were dried over anhydrous sodium sulfate.

E-Homo-28-nor-17α-lup-19(20)-ene-17,22aα-diol (*III*)

Osmium tetroxide (900 mg, 3.54 mmol) was added to a solution of diene[3] *I* (1 190 mg, 2.91 mmol) in ether (150 ml) and the reaction mixture was set aside in the dark at room temperature for 14 days. Lithium aluminium hydride (700 mg, 18.45 mmol) was added, the mixture was refluxed for 4 h and the excess hydride was decomposed with ethyl acetate. The usual work-up gave crude product (1 110 mg) which was purified by chromatography on a silica gel column (80 g). Elution with benzene afforded 680 mg (53%) of diol *III*, m.p. 270 – 272 °C (ethyl acetate), $[\alpha]_D$ −46° (*c* 0.54). For $C_{30}H_{50}O_2$ (442.7) calculated: 81.39% C, 11.38% H; found: 81.22% C, 11.50% H.

22aα-Acetoxy-E-homo-28-nor-17α-lup-19(20)-en-17-ol (*IV*)

Diol *III* (500 mg, 1.13 mmol) was acetylated with a mixture of acetic anhydride and pyridine (1 : 1) at room temperature for 48 h. Yield 440 mg (80%) of monoacetate *IV*, m.p. 233 – 234.5 °C (chloroform–methanol), $[\alpha]_D$ −36° (*c* 0.43). IR spectrum: 3 580, 1 724, 1 250, 1 035. For $C_{32}H_{52}O_3$ (484.7) calculated: 79.28% C, 10.81% H; found: 79.40% C, 11.02% H.

17-Hydroxy-E-homo-28-nor-17α-lup-19(20)-en-22a-one (*V*)

Chromium trioxide (120 mg, 1.20 mmol) was added to a solution of diol *III* (170 mg, 0.38 mmol) in pyridine (15 ml) and the mixture was allowed to stand at room temperature for 2 days with intermittant stirring. After the usual work-up procedure, the product was purified by column chromatography on silica gel (20 g). Elution with benzene afforded 130 mg (77%) of ketol *V*, m.p. 250 – 252.5 °C

(benzene), $[\alpha]_D$ −66° (*c* 0.22). ORD: $[\Theta]_{400}$ −1 040°, $[\Theta]_{328}$ −4 160°, $[\Theta]_{295}$ −440°, $[\Theta]_{263}$ −5 470°. CD spectrum (*c* 0.061): Δε −1.33 (313 nm), Δε −6.74 (227 nm). IR spectrum: 3 550, 1 713, 1 075. For $C_{30}H_{48}O_2$ (440.7) calculated: 81.76% C, 10.98% H; found: 82.03% C, 11.15% H.

17,22aα;19,20-Diepoxy-E-homo-28-nor-17α,19β-lupane (*VI*)

A solution of perbenzoic acid (864 mg, 6.26 mmol) in chloroform was added to a cold solution of olefin[3] *I* (1 070 mg, 2.62 mmol) and the reaction mixture was set aside in a refrigerator overnight. Then it was washed repeatedly with 5% sodium carbonate solution, water, 5% potassium iodide solution, water, 5% sodium sulfite solution and again with water. After drying and evaporation of the solvent, the residue was chromatographed on a column of alumina (50 g, activity IV). Elution with chloroform gave the diepoxide *VI* (730 mg, 63%), m.p. 266 – 269 °C (benzene–hexane), $[\alpha]_D$ −49° (*c* 0.62). IR spectrum: 898, 890. For $C_{30}H_{48}O_2$ (440.7) calculated: 81.76% C, 10.98% H; found: 81.50% C, 11.05% H.

17,22α-Dihydroxy-28,29,30-trinor-17α-gammaceran-19-one (*VII*)

A solution of potassium hydroxide in ethanol (5%, 10 ml) was added to a solution of acetate *VIII* (180 mg, 0.39 mmol) in benzene (30 ml). After standing at room temperature for 1 day, the deposited crystals were collected and washed with ethanol and water. Crystallization from ethanol gave 95 mg (58%) of diol *VII*, m.p. 324 – 326 °C (decomp.). *I*R spectrum (Nujol): 1 705, 1 066. For $C_{27}H_{44}O_3$ (416.6) calculated: 77.83% C, 10.65% H; found: 77.60% C, 10.72% H.

22α-Acetoxy-17-hydroxy-28,29,30-trinor-17α-gammaceran-19-one (*VIII*)
and 22aα-Acetoxy-19,20-epoxy-E-homo-28-nor-17α, 19β-lupan-17-ol (*XIV*)

Ozone was introduced into a solution of olefin *IV* (510 mg, 1.05 mmol) in ethyl acetate (150 ml) under cooling with solid carbon dioxide until the solution became violet. Most of the ethyl acetate was distilled off in vacuo at room temperature and the residue was treated with 80% acetic acid (30 ml) and zinc powder. The reaction mixture was shaken for 1 h and then set aside at room temperature overnight. The remaining zinc was removed by filtration, the filtrate was diluted with ether and the ethereal solution was repeatedly washed with 5% sodium carbonate solution and water. After drying and evaporation, the residue (500 mg) was chromatographed on a column of silica gel (75 g). Elution with benzene afforded 150 mg (28%) of epoxy derivative *XIV*, m.p. 261 –265 °C (benzene–ethanol), $[\alpha]_D$ −21° (*c* 0.58). IR spectrum: 3 540, 1 729, 1 252, 1 042, 860. For $C_{32}H_{52}O_4$ (500.7) calculated: 76.75% C, 10.47% H; found: 76.74% C, 10.36% H. Further elution with the same solvent gave 300 mg (62%) of ketone *VIII*, m.p. 257.5 – 259 °C (benzene–ethanol), $[\alpha]_D$ −57° (*c* 0.68). ORD: $[\Theta]_{400}$ −470°, $[\Theta]_{320}$ −6 790°, $[\Theta]_{313}$ −5 380°, $[\Theta]_{309}$ −5 620°, $[\Theta]_{297}$ 0°, $[\Theta]_{275}$ +6 320°, $[\Theta]_{250}$ 3 740°. IR spectrum: 3 600, 3 430, 1 728, 1 716, 1 245, 1 036. For $C_{29}H_{46}O_4$ (458.7) calculated: 75.94% C, 10.11% H; found: 76.08% C, 10.01% H.

17-Hydroxy-28,29,30-trinor-17α-gammacerane-19,22-dione (*IX*)

A solution of chromium trioxide (150 mg, 1.50 mmol) in *N*,*N*-dimethylformamide (8 ml) was added to a solution of diol *VII* (150 mg, 0.36 mmol) in the same solvent (30 ml). The reaction mixture was allowed to stand at room temperature for 4 days. The usual work-up afforded 90 mg (60%) of ketol *IX*, m.p. 273 – 275 °C (chloroform–methanol), $[\alpha]_D$ −49° (*c* 0.53). CD spectrum (*c* 0.054): Δε −1.32 (316 nm), Δε −2.05 (306 nm), Δε −2.13 (297 nm). IR spectrum: 3 560, 3 425, 1 717, 1 050. For $C_{27}H_{42}O_3$ (414.6) calculated: 78.21% C, 10.21% H; found: 77.95% C, 10.15% H.

19,20-Epoxy-E-homo-28-nor-17α,19β-lupan-17-ol (*X*)

Lithium aluminium hydride (500 mg, 13.18 mmol) in ether (100 ml) was added to a solution of diepoxide *VI* (650 mg, 1.47 mmol) in benzene (10 ml). After reflux for 2 h, the unreacted hydride was destroyed with ethyl acetate. The usual work-up gave alcohol *X* (500 mg, 77%), m.p. 289 – 293 °C (benzene–ethyl acetate), $[\alpha]_D$ −18.5° (*c* 0.43). IR spectrum: 3 430, 1 074, 908, 888. For $C_{30}H_{50}O_2$ (442.7) calculated: 81.39% C, 11.38% H; found: 81.22% C, 11.37% H.

19,20-Epoxy-E-homo-28-nor-17α,19β-lupan-22aα-ol (*XI*)

3-Chloroperbenzoic acid (60%, 100 mg, 0.35 mmol) was added to a cold solution of olefin[4] *II* (100 mg, 0.23 mmol) in chloroform (10 ml) and the solution was allowed to stand for 24 h in a refrigerator. The work-up procedure was the same as described for the preparation of diepoxide *VI* and the obtained product was purified by preparative thin-layer chromatography (200 × 200 × 0.7 mm layer) in heptane–ether (9 : 1) to yield 62 mg (60%) of epoxide *XI*, m.p. 251 – 252 °C (chloroform–methanol), $[\alpha]_D$ −6° (*c* 0.55). IR spectrum: 3 595, 1 031, 881, 862. For $C_{30}H_{50}O_2$ (442.7) calculated: 81.39% C, 11.38% H; found: 81.55% C, 10.19% H.

19,20-Epoxy-E-homo-28-nor-17α,19β-lupan-22aα-yl Acetate (*XII*)

Alcohol *XI* (40 mg, 0.09 mmol) was acetylated under the same conditions as the diol *III*. The yield of the title compound *XII* was 30 mg (69%), m.p. 225 – 227 °C (chloroform–methanol), $[\alpha]_D$ +8° (*c* 0.46). IR spectrum: 1 723, 1 250, 1 028, 884, 861. For $C_{32}H_{52}O_3$ (484.7) calculated: 79.28% C, 10.81% H; found: 79.48% C, 10.75% H.

19,20-Epoxy-E-homo-28-nor-17α,19β-lupane-17,22aα-diol (*XIII*)

Ethanolic potassium hydroxide (5 ml of 5% solution) was added to a solution of acetate *XIV* (50 mg, 0.10 mmol) in ethanol (20 ml) and the mixture was refluxed for 4 h. The usual work-up afforded 40 mg (87%) of diol *XIII*, m.p. 252 – 255 °C (chloroform–methanol), $[\alpha]_D$ −16° (*c* 0.47). IR spectrum: 3 525, 1 040, 879. For $C_{30}H_{50}O_3$ (458.7) calculated: 78.55% C, 10.99% H; found: 78.70% C, 10.85% H.

19,20-Epoxy-17-hydroxy-E-homo-28-nor-17α,19β-lupan-22a-one (*XV*)

Diol *XIII* (40 mg, 0.09 mmol) was oxidized with chromium trioxide (30 mg, 0.30 mmol) in pyridine (5 ml) under the same conditions as the diol *III*. The crude product was chromatographed on a column of silica gel (5 g). Elution with benzene–ether (9 : 1) afforded 35 mg (88%) of ketol *XV*, m.p. 301 – 304 °C (ether–hexane), $[\alpha]_D$ −64° (*c* 0.64). IR spectrum: 3 510, 1 715, 1 036, 863, 853. For $C_{30}H_{48}O_3$ (456.7) calculated: 78.89% C, 10.59% H; found: 78.60% C, 10.44% H.

Epoxidation of Olefin *XVI*

A solution of perbenzoic acid (202 mg, 1.46 mmol) in benzene (10 ml) was added to a solution of olefin[1] *XVI* (500 mg, 1.22 mmol) in benzene (15 ml). After standing at room temperature for 5 h, the reaction mixture was diluted with ether and processed as described for the preparation of the diepoxide *VI*. Crystallization from benzene–ethanol gave 470 mg (90%) of epoxide *XVII*, m.p. 170 – 174 °C, $[\alpha]_D$ +30° (*c* 0.64). IR spectrum: 915, 897. For $C_{30}H_{50}O$ (426.7) calculated: 84.44% C, 11.81% H; found: 84.18% C, 11.95% H.

E-Homo-28-nor-17α-lupan-17-ol (*XVIII*) and E-Homo-28-nor-17β-lupan-17-ol (*XXIV*)

A mixture of epoxide *XVII* (230 mg, 0.54 mmol), lithium aluminium hydride (200 mg, 5.27 mmol) and ether (60 ml) was refluxed for 12 h. After decomposition of the reaction mixture with ethyl acetate and the usual work-up, the obtained mixture of alcohols *XVIII* and *XXIV* (200 mg) was separated by column chromatography on alumina (50 g, activity *III*). Elution with light petroleum–ether (99 : 1) gave 90 mg (39%) of alcohol *XXIV*, m.p. 137.5 – 139.5 °C (benzene–ethanol), $[\alpha]_D$ +26° (*c* 0.66). IR spectrum: 3 620, 1 090. For $C_{30}H_{52}O$ (428.7) calculated: 84.04% C, 12.23% H; found: 83.76% C, 12.40% H.

Further elution with the same solvent mixture afforded 80 mg (35%) of alcohol *XVIII*, m.p. 222.5 – 223.5 °C (ether–hexane), $[\alpha]_D$ +37° (*c* 0.64). IR spectrum: 3 615, 1 090, 1 031. For $C_{30}H_{52}O$ (428.7) calculated: 84.04% C, 12.23% H; found: 83.91% C, 12.20% H.

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