# THE SYNTHESIS AND THE MASS SPECTRA OF 28,29,30-TRINOR-OLEANANE DERIVATIVES WITH A DOUBLE BOND IN THE RING E OR D*

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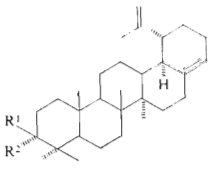
A series of 28,29,30-trinor-18α-oleanane derivatives with two double bonds — 17(22) and 20(29) — was prepared. The position of the 17(22) double bond was demonstrated by partial hydrogenation of the diene on tris-triphenylphosphinerhodium chloride and by comparison of the product with an authentic sample. The mass spectra of the series of dienes *I*—*IV* and monoenes *VI*—*X* are discussed.

The preparation of 28,29,30-trinor-18α-oleanane derivatives was carried out by Vesterberg[1] without a structure determination; the preparation and the structure proposal for derivatives with a saturated side chain was performed in our laboratory[2,3]. Since a rigorous structure proof of Vesterberg's products has not yet been carried out and since the mass spectra of these derivatives with a double bond in the position 17(22) or 16 display a distinct fragmentation, we decided to supplement their series by so far undescribed substances and to study the mass spectra of the whole series more closely.

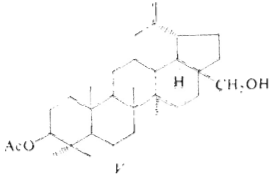
Dehydration of 3β-acetoxy-20,29-lupen-28-ol (*V*) with phosphorus pentachloride[1] gave the compound *III* from which derivatives *I*, *II* and *IV*, differently substituted in the ring A, were prepared using conventional procedures. Although dehydration with phosphorus pentachloride gives the required product in an only 50% yield, it was impossible to use the solvolysis of the corresponding tosylate in this case (which gives up to a 92% yield)[2], because under the solvolysis conditions a shift of the double bond in the isopropenyl side chain[4] takes place. According to the $^1$H NMR spectra the original double bond in the isopropenyl side chain remains preserved in dienes *I*—*IV* (the signals at 1·73 to 1·77 ppm for the methyl group on $C_{(20)}$ and the pairs of multiplets at 4·64 to 4·66 ppm and 4·71 to 4·73 ppm for $CH_2$=C). This terminal double bond is also visible in the IR spectra, from the absorption at 1 646—1 654 and 889—892 cm$^{-1}$. The second double bond is evidenced

* Part LXVII in the series Triterpenes; Part LXVI: This Journal *48*, 649 (1983).

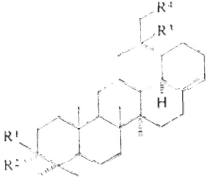
by the absorption at 1 671–1 680 $cm^{-1}$. In the $^1H$ NMR spectra the signal of 1 proton of this double bond is evident at 5·32 to 5·35 ppm which appears as a broad



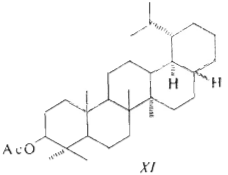
*I*, $R^1 = R^2 = H$
*II*, $R^1 = OH$, $R^2 = H$
*III*, $R^1 = OAc$, $R^2 = H$
*IV*, $R^1 + R^2 = O$



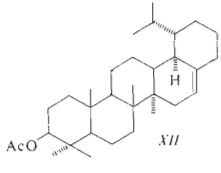
*V*



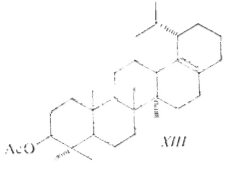
*VI*, $R^1 = R^2 = R^3 = R^4 = H$
*VII*, $R^1 = OAc$, $R^2 = R^3 = R^4 = H$
*VIII*, $R^1 + R^2 = O$; $R^3 = R^4 = H$
*IX*, $R^1 = R^2 = H$, $R^3 = R^4 = {}^2H$
*X*, $R^1 = OAc$, $R^2 = H$, $R^3 = R^4 = {}^2H$



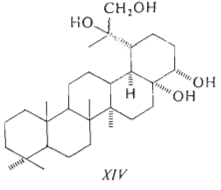
*XI*



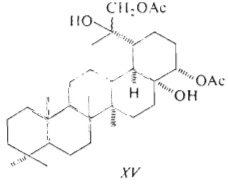
*XII*



*XIII*



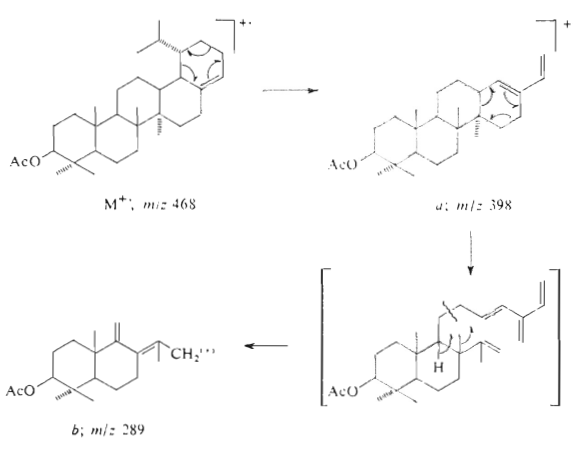
*XIV*



*XV*

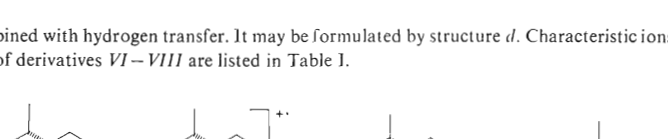
triplet or even multiplet. Hydroxylation of diene *I* with osmium tetroxide gave tetrol *XIV*. The configuration of its hydroxy groups in positions 17 and 22 is supposed to be α on the basis of ref.[3]. On acetylation of tetrol *XIV* diacetate *XV* was obtained, the formation of which shows the presence of two hydroxy groups on tertiary carbons. The position of the trisubstituted double bond was demonstrated by comparison of the products *VI* and *VII*, obtained by hydrogenation of the double bond in the isopropenyl group of derivative *I* or *III*, respectively, on tris-triphenylphosphinerhodium chloride (according to out previous paper[5]), with known substances[2]. Thus it was shown unequivocally that the double bond, formed on dehydration of betulin monoacetate *V* with phosphorus pentachloride, was in the position 17(22). By this the structure of the derivatives obtained by Vesterberg[1] was also demonstrated.

From the mass spectra of the series of anhydro derivatives with the saturated side chain, *VI*–*X* (ref.[2,5]) it is evident that the double bond in the position 17(22) initiates the formation of distinct ions in the region of medium masses of the spectrum. This is also evident from the mass spectrum of the fully saturated derivative *XI* (ref.[2]) which was prepared on hydrogenation of diene *III*, and where these distinct ions are completely absent. In the region of higher masses in all the spectra of the series of derivatives *VI*–*X* there are ions corresponding to the losses of the methyl radical, ethylene molecule, the radical $C_3H_7^{\bullet}$ (isopropyl side chain), the acetic acid molecule in the case of acetoxy derivative *VII*, and of their combinations. The proof that the ions $[M-C_3H_7]^+$ are due to the loss of the isopropyl side chain follows from the spectra of deuterio derivatives *IX* and *X*. This is in contradiction with the experience with lupane derivatives where the loss $[M-C_4H_7]^+$, considered as a loss of the isopropyl group, is a combined loss of an ethylene molecule and a methyl radical, while the isopropyl group is not split off[6]. The proposal for the fragmentation of derivatives *VI*–*X* is illustrated in Scheme 1 by the example of the acetoxy derivative *VII*. It may be assumed that the retro-Diels–Alder cleavage in the ring E of the molecular ion and the splitting off of the molecule $C_5H_{10}$ under formation of ion *a*, *m/z* 398 is operative in this example (the ions of type *a* are represented in all spectra of the series, but they are weak). This transition could not be demonstrated by the Direct Analysis of the Daughter Ions method. An analogous cleavage is also assumed for the ion *a*. The a cleavage of the bond between the carbons 11 and 12 (allylic to the double bond) takes place, followed by the splitting off of the methyl radical and a hydrogen atom transfer. Thus the dominant ion of the spectrum is formed which can be termed as *b*, *m/z* 289. It loses a molecule of acetic acid under formation of the ion *c*, *m/z* 229. The ion *c* is also formed in an analogous manner from the ion $(M-CH_3COOH)^{+\bullet}$, *m/z* 408. Further the spectra of the series contain intensive known ions belonging to the rings A and B, *i.e.* *m/z* 191 in 3-deoxy-, *m/z* 189 and 249 in 3-acetoxy- and *m/z* 205 in 3-oxo derivative[7]. The fragment *m/z* 135 in derivatives *VI*–*VIII* may be assigned to the ring E, as also can the fragment *m/z* 137 in derivatives *IX* and *X*, which is formed by cleavage of the ring D, com-



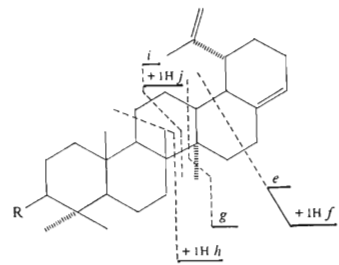

SCHEME 1

bined with hydrogen transfer. It may be formulated by structure *d*. Characteristic ions of derivatives *VI* – *VIII* are listed in Table I.




The fragmentation of dienes *I* – *IV* is distinctly richer in comparison with the fragmentation of derivatives *VI* – *VIII* which do not have a double bond in the side chain. The fundamental type of fragmentation, *i.e.* the ions of the type *a*, *b*, and *c* are equal here as in derivatives *VI* – *VIII*, the same as the simple and the combined losses in the region of higher masses. However, in addition to them the dienes contain a number of intensive ions belonging to the ring E or also D, formed by the

cleavage of the rings C or D, which are completely absent in the monoene. The types of these ions follow from Scheme 2. The characteristic ions of derivatives *I*–*VV* are presented in Table II. Further known[7] prominent ions of the derivatives *I*–*II* are the following: *m/z* 191 in 3-deoxy-, *m/z* 249 and 189 in 3-acetoxy-, *m/z* 207 and 189 in 3-hydroxy-, and *m/z* 205 in 3-oxo derivatives.




SCHEME 2

TABLE I
Characteristic ions (*m/z*, %) of derivatives *VI*–*VIII*

| Ion | *VI* | *VII* | *VIII* |
|---|---|---|---|
| *a* | 340 (4) | 398 (2) | 354 (2) |
| *b* | 231 (80) | 289 (72) | 245 (100) |
| *c* | — | 229 (43) | — |

TABLE II
Characteristic ions (*m/z*) of derivatives *I*–*IV*

| Ions | *a* | *b* | *c* | *e* | *f* | *g* | *h* | *i* | *j* | *k* | *l* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *I* | 340 | 231 | — | 134 | 135 | 175 | 216 | 202 | 203 | 191 | — |
| *II* | 356 | 247 | 229 | 134 | 135 | 175 | 216 | 202 | 203 | 207 | 189 |
| *III* | 398 | 289 | 229 | 134 | 135 | 175 | 216 | 202 | 203 | 249 | 189 |
| *IV* | 354 | 245 | — | 134 | 135 | 175 | 216 | 202 | 203 | 205 | — |

After the preparation of anhydro derivative *VII* (ref.[2]) from the mother liquors isomeric derivatives *XII* and *XIII* were obtained by column chromatography on silica gel with silver nitrate. The structure of derivative *XII* is also confirmed by its mass spectrum, in addition to the $^1$H NMR spectrum, where one proton on the double bond is evident. Characteristic for the mass spectrum is the ion *m*, *m/z* 150 ($C_{11}H_{18}$), which is formed by the retro-Diels–Alder cleavage of the ring D. A similar fragmentation was also observed in 16-lupene derivatives[8]. In the $^1$H NMR spectrum of derivative *XIII* no proton on the double bond is observed. In the IR spectrum only an acetoxyl group is evident. The mass spectra of 17(18)-oleanane derivatives were already studied[7] and the characteristic ions described are formed by retro-Diels–Alder cleavage of the ring D. Analogous ions *n* and *o* are also present in the mass spectrum of derivative *XIII* in addition to further distinct ions in the region of medium masses, not observed in the analogues in ref.[7]. A proposal of their structure would have only a speculative character.

## EXPERIMENTAL

The melting points were measured on a Kofler block and they have not been corrected. Optical rotation was measured in chloroform (unless stated otherwise) on an automatic ETL-NPL Bendix-Ericsson) polarimeter, with a $\pm 2°$ accuracy. The infrared spectra were measured in chloroform on a UR 10, Zeiss Jena, instrument, the $^1$H NMR spectra in deuteriochloroform, using tetramethylsilane as internal reference, on a Varian HA 100 instrument. Chemical shifts are given in ppm, $\delta$-scale. The mass spectra were measured on a Varian MAT 311 instrument, at 70 eV energy of the ionizing electrons and 1 mA of the ionizing current. Ion source temperature 200°C, temperature of the direct inlet system 90—160°C. The composition of the ions (where it is mentioned) was measured by the high resolution method and the discussed geneses of the ions were checked by the Direct Analysis of Daughter Ions technique. Samples for analysis were dried at 100°C in a vacuum, over $P_2O_5$, for 8—10 h. Compounds *VIII* and *XI* were prepared in paper[2] and *IX* and *X* in paper[5].

3β-Acetoxy-19α-isopropenyl-28,29,30-trinor-18α-olean-17(22)-ene (*III*)

Alcohol *V* (11 g) was added in small portions under shaking to a suspension of phosphorus pentachloride (9·8 g) in light petrcleum (500 ml) and the mixture was allowed to stand at room temperature overnight. The precipitate was filtered off and the light petroleum solution washed with water, 5% sodium carbonate solution and water, then dried by filtration through a layer of aluminum oxide and evaporated. The residue (10·8 g) was chromatographed on a column of alumina (150 g). Elution with benzene (400 ml) gave 5·8 g (55%) of derivative *III*, m.p. 210 to 212·5°C (chloroform–ethyl acetate), $[\alpha]_D$ −15° (*c* 1·3). IR spectrum: 1 728, 1 260, 1 030, (CH$_3$.COO), 1 677, 1 647, 890 (C=C) cm$^{-1}$. $^1$H NMR spectrum: 0·84 (4β-CH$_3$); 0·85 (4α-CH$_3$); 0·86 (10β-CH$_3$); 0·95 (14α-CH$_3$); 1·04 (8β-CH$_3$); 1·76 bs (20-CH$_3$); 2·025 (3-OAc); 4·65 m + + 4·72 m (CH$_2$=C); 4·49 m (3α-H); 5·35 bt (22-H). Mass spectrum, *m/z* (composition, %): 466 (M$^+$, $C_{32}H_{50}O_2$, 18), 451 ($C_{31}H_{47}O_2$, 3), 423 ($C_{29}H_{43}O_2$, 3), 406 ($C_{30}H_{46}$, 12), 398 ($C_{27}H_{42}O_2$, 2), 391 ($C_{29}H_{43}$, 6), 363 ($C_{27}H_{39}$, 10), 289 ($C_{19}H_{29}O_2$, 19), 249 ($C_{16}H_{25}O_2$, 17), 229 ($C_{17}H_{25}$, 34), 216 ($C_{16}H_{24}$, 40), 203 ($C_{15}H_{23}$, 73), 202 ($C_{15}H_{22}$, 50), 189 ($C_{14}H_{21}$, 100), 175 ($C_{13}H_{19}$, 65), 135 ($C_{10}H_{15}$, 73), 134 ($C_{10}H_{14}$, 95); for $C_{32}H_{50}O_2$ (466·6) calculated: 82·34% C, 10·80% H; found: 82·50% C, 10·86% H.

3β-Hydroxy-19α-isopropenyl-28,29,30-trinor-18α-olean-17(22)-ene (*II*)

Hydrolysis of acetate *III* (2·5 g) by 7 h refluxing in a benzene-ethanolic solution of potassium hydroxide (1 g) gave 1·96 g of hydroxy derivative *II*, m.p. 184–185°C (chloroform–methanol), $[\alpha]_D$ −29° (*c* 0·33). IR spectrum: 3 610, 3 450, 1 031 (OH), 1 671, 1 646, 889 (C=C) $cm^{-1}$. Mass spectrum, *m/z* (%): 424 (21), 409 (5), 406 (6), 391 (5), 363 (8), 356 (5), 247 (29), 229 (24), 216 (38), 207 (94), 203 (47), 202 (35), 189 (53), 175 (59), 135 (100), 134 (100). For $C_{30}H_{48}O$ (424·7) calculated: 84·84% C, 11·39% H; found: 84·26% C, 11·34% H.

3-Oxo-19α-isopropenyl-28,29,30-trinor-18α-olean-17(22)-ene (*IV*)

Chromium trioxide (3 g) was added in portions to a solution of hydroxy derivative *II* (1·4 g) in pyridine (50 ml) and the mixture was allowed to stand at room temperature for 8 days. After dilution with water the product was extracted with ether. The ethereal solution was washed with water, dilute hydrochloric acid (1 : 4), water, and a sodium carbonate solution (5%). After drying over sodium sulfate the filtrate was evaporated and the residue (1·25 g) crystallized from chloroform–methanol. The product, oxo derivative *IV*, had m.p. 144–145°C, $[\alpha]_D$ +10° (*c* 1·3). IR spectrum: 1 693 (C=O), 1 648, 892 (C=C) $cm^{-1}$. $^1H$ NMR spectrum: 0·93 d, $J_{l.r.}$ = 0·6 Hz (10β-$CH_3$); 0·98 (14α-$CH_3$); 1·02 (4β-$CH_3$); 1·06 (4α-$CH_3$); 1·08 (8β-$CH_3$); 1·77 bs (20-$CH_3$); 2·46 m (2-$H_2$); 4·66 m + 4·73 mm ($CH_2$=C); 5·32 bt (22-H). Mass spectrum, *m/z* (%): 422 (24), 407 (8), 354 (6), 245 (20), 216 (15), 205 (45), 203 (82), 202 (28), 175 (51), 135 (48), 134 (100). For $C_{30}H_{46}O$ (422·7) calculated: 85·24% C, 10·97% H; found: 85·00% C, 10·94% H.

19α-Isopropenyl-28,29,30-trinor-18α-olean-17(22)-ene (*I*)

Hydrazine hydrate (85%, 10 ml) and then ethanol were added to a solution of oxo derivative *IV* (3·0 g) in benzene (25 ml) until a homogeneous solution was obtained. The mixture was refluxed for 5 h and then concentrated to half its volume. Additional hydrazine hydrate (85%, 5 ml) was then added to the concentrated solution, followed by diethylene glycol (40 ml) and potassium hydroxide (4 g). The mixture was heated slowly to 225°C and kept at this temperature for 3 h. After cooling it was diluted with water, the product was extracted with ether, the ethereal solution washed with water, dilute hydrochloric acid (1 : 4), again with water and sodium carbonate solution (5%). After drying over sodium sulfate and filtration the solution was concentrated and the dry residue dissolved in cyclohexane. This solution was filtered through a layer of aluminum oxide (4 g). Yield, 2·24 g (77%) of 3-deoxy derivative *I*, m.p. 149–150°C (ethyl acetate), $[\alpha]_D$ −26° (*c* 1·3). IR spectrum: 1 680, 1 654, 892 (C=C) $cm^{-1}$. $^1H$ NMR spectrum: 0·755 (4β-$CH_3$); 0·81 (4α-$CH_3$, 10β-$CH_3$); 0·91 (14α-$CH_3$); 1·02 (8β-$CH_3$); 1·73 bs (20-$CH_3$); 4·64 m + 4·71 m ($CH_2$=C); 5·34 m, $W_{1/2}$ = 10 Hz (22-H). Mass spectrum, *m/z* (%): 408 (15), 393 (5), 365 (3), 340 (3), 231 (30), 216 (32), 203 (17), 202 (23), 191 (100), 175 (24), 134 (42). For $C_{30}H_{48}$ (408·7) calculated: 88·16% C, 11·84% H; found: 88·06% C, 11·64% H.

19α-Isopropyl-28,29,30-trinor-18α-olean-17(22)-ene (*VI*)

Tris(triphenylphosphine)rhodium chloride, prepared according to ref.[9] (50 mg) was added to a solution of deoxy derivative *I* (50 mg) in a mixture of benzene and ethanol (4 : 1) (5 ml) and the mixture was stirred under hydrogen for 3 h. After evaporation of the solvents the residue was extracted with 5 ml of hexane. The hexane solution was filtered through a small column of alumina, the filtrate was evaporated and the residue crystallized. Dihydro derivative *VI* (45 mg) was thus obtained, m.p. 181–183°C (chloroform–methanol), $[\alpha]_D$ −46° (*c* 0·63), which was identical with an authentic sample prepared earlier[2]. Mass spectrum, *m/z* (%): 410 ($M^+$, 7), 395 (5), 367 (8), 340 (4), 231 (80), 191 (100), 135 (17).

3β-Acetoxy-19α-isopropyl-28,29,30-trinor-18α-olean-17(22)-ene (*VII*)

Using the same procedure as in the case of deoxy derivative *I*, acetate *II* (50 mg) was hydrogenated on tris(triphenylphosphine)rhodium chloride (50 mg) to dihydro derivative *VII* (42 mg), m.p. 203–207°C (chloroform–methanol), $[\alpha]_D$ −30° (*c* 0·36), identical with an authentic sample prepared earlier[2]. Mass spectrum, *m/z* (composition, %): 468 ($M^+$, $C_{32}H_{52}O_2$, 8·5), 453 ($C_{31}H_{49}O_2$, 8·5), 453 ($C_{31}H_{49}O_2$, 4), 425 ($C_{29}H_{45}O_2$, 7), 408 ($C_{30}H_{48}$, 14), 398 (2), 393 ($C_{29}H_{45}$, 7), 365 ($C_{27}H_{41}$, 35), 289 ($C_{19}H_{29}O_2$, 72), 249 ($C_{16}H_{25}O_2$, 16), 229 ($C_{17}H_{25}$, 43), 189 ($C_{14}H_{21}$, 85), 135 ($C_{10}H_{15}$, 52), 43 ($C_2H_3O$, 100).

3β-Acetoxy-19α-isopropyl-28,29,30-trinor-18α-olean-17-ene (*XIII*)
and 3β-Acetoxy-19α-isopropyl-28,29,30-trinor-18α-olean-16-ene (*XII*)

The mother liquors, after the preparation of anhydro derivative *VII* (ref.[2]) (0·88 g), were chromatographed on 75 g of silica gel impregnated with 10% of silver nitrate. Elution with hexane, containing 2% of ether, (330 ml) gave 70 mg of derivative *XIII*, m.p. 191–194°C (benzene–hexane), $[\alpha]_D$ +36° (*c* 0·60). IR spectrum: 1 723, 1 258, 1 030 ($OCOCH_3$) $cm^{-1}$. $^1H$ NMR spectrum: 0·84 (2 × $CH_3$); 0·87 ($CH_3$); 0·93 ($CH_3$); 0·96 ($CH_3$); 0·84 d, $J$ = 6 Hz and 0·86 d, $J$ = 6 Hz (19α-$CH(CH_3)_2$); 2·02 (3-OAc), 4·48 m (3α-H). Mass spectrum, *m/z* (%): 468 (22), 453 (3), 425 (40), 408 (8), 365 (35), 231 (34), 205 (70), 204 (75), 191 (75), 189 (65), 177 (90), 175 m(75), 163 (40), 161 (100). For $C_{32}H_{52}O_2$ (468·7) calculated: 81·99% C, 11·18% H; found: 81·75% C, 11·34% H.

On further elution with 2% ether in hexane 200 mg of derivative *XII*, were obtained m.p. 233·5–234·5°C (benzene–hexane), $[\alpha]_D$ +86° (*c* 0·67). IR spectrum: 1 725, 1 260, 1 029 ($OCOCH_3$), 1 681 (C=C) $cm^{-1}$. $^1H$ NMR spectrum: 0·83 ($CH_3$), 0·84 ($CH_3$); 0·85 ($CH_3$); 0·87 ($CH_3$); 0·95 ($CH_3$); 0·80 d, $J$ = 6 Hz and 0·91 d, $J$ = 6 Hz (19α-$CH(CH_3)_2$); 2·02 (3-$OCOCH_3$), 4·48 m (3α-H); 5·25 bd, $J_{15,16}$ = 6·2 ± 1·5 Hz (16-H). Mass spectrum, *m/z* (%): 468 ($M^+$, 28), 453 (5), 425 (20), 408 (18), 393 (10), 365 (21), 249 (10), 204 (51), 189 (100), 150 ($C_{11}H_{18}$, 88). For $C_{32}H_{52}O_2$ (468·7) calculated: 81·99% C, 11·18% H; found: 81·80% C, 11·33% H.

Tetrol *XIV* and its Acetylation

Osmium tetroxide (900 mg) was added to a solution of diene *I* (690 mg) in anhydrous ether (300 ml) and allowed to stand for 5 h at room temperature. An aqueous solution (20 ml) of mannitol (1 g) was added, followed by potassium hydroxide (1 g) and ethanol (100 ml). The mixture was concentrated and tetrol *XIV* (320 mg) crystallized out, m.p. 282–285°C, $[\alpha]_D$ +34° (*c* 0·49, ethanol). IR spectrum (nujol): 1 048, 1 067, 1 087 (C–O) $cm^{-1}$. For $C_{30}H_{52}O_4$ (476·7) calculated: 75·58% C, 11·00% H; found: 75·26% C, 10·86% H. Diacetate *XV* was prepared on acetylation of tetrol *XIV* with acetic anhydride in pyridine. M.p. 245–249°C (chloroform–methanol), $[\alpha]_D$ +27° (*c* 0·31). IR spectrum: 1 732, 1 248 ($OCOCH_3$), 1 057, 1 065, 1 087 (C–O), 3 400, 3 580 (OH) $cm^{-1}$. For $C_{34}H_{56}O_6$ (560·8) calculated: 72·82% C, 10·06% H; found: 72·58% C, 9·88% H.

Mass Spectrum

*VIII*: *m/z* (%): 424 ($M^+$, 7·5), 409 (4), 381 (13), 363 (2), 354 (2), 245 (100), 205 (45), 135 (38);

*IX*: *m/z* (%): 412 ($M^+$, 6), 397 (4), 367 (10), 340 (2), 231 (78), 191 (100). Distribution of deuterium: $d_0$ 12%, $d_1$ 19%, $d_2$ 63%, $d_3$ 0%, $d_4$ 6%.

*XI*: *m/z* (%): 470 ($M^+$, 30), 455 (3·5), 427 (5), 410 (24), 395 (11), 367 (11), 249 (48), 189 (100).

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REFERENCES

1. Vesterberg R.: Chem. Ber. *65*, 1305 (1932).
2. Vystrčil A., Křeček V., Buděšínský M.: This Journal *39*, 2494 (1974).
3. Vystrčil A., Křeček V., Buděšínský M.: This Journal *39*, 3131 (1974).
4. Vystrčil A.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1965.
5. Protiva J., Lepša L., Klinotová E., Klinot J., Křeček V., Vystrčil A.: This Journal *46*, 2734 (1981).
6. Protiva J.: Unpublished results
7. Budzikiewicz H., Wilson J. M., Djerassi C.: J. Amer. Chem. Soc. *85*, 3688 (1963).
8. Baddeley G. V., Fookes C. R. J., Nigam S. K.: Aust. J. Chem. *29*, 2707 (1976).
9. Voelter W., Djerassi C.: Chem. Ber. *101*, 58 (1968).

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