E-SECO-ACIDS OF PENTACYCLIC TRITERPENOIDS. OXIDATIVE CLEAVAGE OF RING E IN 3β-ACETOXY-21-OXO--18α,19β*H*-URSAN-28→20β-OLIDE*

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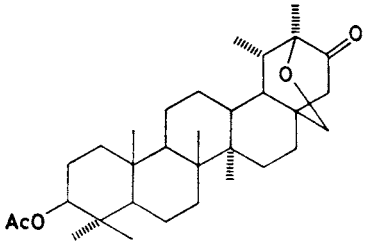
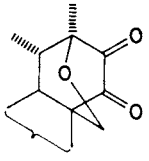
Oxidative cleavage of 3β-acetoxy-22-hydroxymethylene-21-oxo-18α,19β*H*-ursan-28→20β-olide (*VII*) and 3β-acetoxy-21,22-dioxo-18α,19β*H*-ursan-28→20β-olide (*VIII*) afforded primarily the E-seco-acid *XII* which was converted into acids *XVI* and *XX*, isomeric at the C(17) carbon atom. Configuration of these acids has been determined.

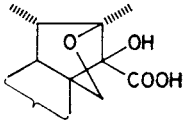
In connection with the preparation of triterpenoid E-seco-acids of potential antibacterial activity, we studied[1-3] oxidation reactions of the oxabicyclo[2.2.2]octane and oxabicyclo[2.2.1]heptane systems in the ring E of pentacyclic triterpenoids derived from 18α,19β*H*-ursane. These compounds exhibited unusual reactions caused by the considerably strained bridged systems in the ring E. In this paper we describe the preparation and reactions of E-seco-derivatives formed by C(21)—C(22) bond cleavage in 21,22-disubstituted 18α,19β*H*-ursan-28→20β-olide derivatives. As starting material we used 3β-acetoxy-21-oxo-18α,19β*H*-ursan-28→20β-olide (*IV*) prepared according to the literature[4]. For comparison, we carried out some reactions with the analogous 3β-acetoxy-20β,28-epoxy-18α,19β*H*-ursan-21-one (*I*; for preparation see ref.*4*), containing an ether instead of lactone bridge in the ring E.



I



II



III

* Part LXXXIV in the series Triterpenes; Part LXXXIII: Collect. Czech. Chem. Commun. *52*, 1052 (1987).

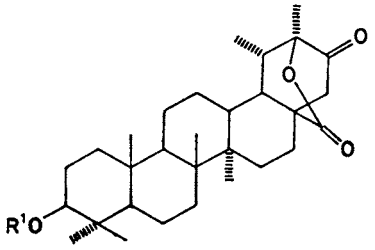
The oxidative cleavage of ring E was carried out with 22-hydroxymethylene derivative *VII* and diketone *VIII*. The compound *VII* was prepared from ketone *IV* by a procedure used previously[2] for the analogous compound *I*: Condensation of ketone *IV* with ethyl formate, catalyzed with sodium hydride, afforded ketone *V* which was further converted to the diacetate *VI*. Partial hydrolysis of *VI* with hydrochloric acid in acetone furnished the desired derivative *VII*. The diketone *VIII* was obtained by oxidation of *IV* with selenium dioxide in a mixture of acetic acid and dioxane. The same procedure was used in the preparation of diketone *II* from ketone *I*.

Compared with ether *II*, the lactone *VIII* is substantially more reactive: in chloroform solutions in the presence of polar solvents (*e.g.* acetone or methanol) or sorbents (alumina or silica gel) it decomposes into a mixture of unidentified products. During attempted chromatographic purification on silica gel we observed in some cases a spontaneous exothermic reaction leading to probably dimeric products (according to ^{1}H and ^{13}C NMR spectra). Also, the benzilic rearrangement of diketone *VIII* was unusually facile: in a mixture of chloroform and methanol, *VIII* afforded quantitatively the known[3] methyl ester *X* with contracted E-ring merely on standing for several hours with sodium hydrogen carbonate at room temperature. No reaction was observed under these conditions with the ether *II*. On heating with potassium hydroxide in benzene–ethanol both compounds *II* and *VIII* react to give the known[3] hydroxy acids *III* and *IX*, respectively. This facile benzilic rearrangement of diketone *VIII* can now explain also the observed[1,3] different course of alkaline autooxidation of ether *I* and lactore *IV*: whereas, as expected, the ether *I* was predominantly oxidized to the E-seco-diacid[1], oxidation of the analogous lactore *IV* afforded no E-seco-derivatives[3] (such as diacid *XII* and products of its conversion) and all the originally formed diketone was immediately rearranged to acid *IX*.

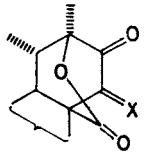
Oxidative cleavage of compound *VII* was done with chromium trioxide in acetic acid at room temperature, diketone *VIII* was oxidized with Jones reagent. In both cases we obtained three products: diacid *XII*, acid *XVI*, and the known[3] dilactone *XXII*. The diacid *XII* was best prepared by oxidation of *VIII* with peroxyacetic acid which gave the other two products in negligible amounts. The use of 3-chloroperoxybenzoic acid was less advantageous because of difficult removal of 3-chlorobenzoic acid from the reaction mixture.

Evidently, the oxidative cleavage leads primarily to diacid *XII* characterized also as its methyl ester *XIII*. The other two compounds are then formed from *XII* by decarboxylation or oxidative decarboxylation combined with formation of the lactone ring (see *e.g.* ref.[5]). On heating with *p*-toluenesulfonic acid in acetic anhydride, diacid *XII* was decarboxylated to give acid *XVI*. Treatment with an alkali metal hydroxide in benzene–ethanol resulted in hydrolysis of the ester groups and decarboxylation with partial isomerization at C(17). The obtained mixture of isomeric acids *XIV* and *XVIII* was separated by chromatography on silica gel and the acids were

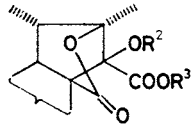
characterized as methyl esters *XV* and *XIX*, acetates *XVI* and *XX*, and ester-acetates *XVII* and *XXI*. A mixture of *XIV* and *XVIII* was also formed in hydrolysis of the individual methyl esters *XVII* and *XXI* as well as in the base-catalyzed acid-forming



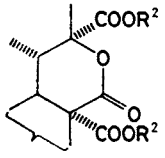
IV, R^1 = Ac



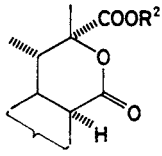
V, R^1 = H; X = CHOH
VI, R^1 = Ac; X = CHOAc
VII, R^1 = Ac; X = CHOH
VIII, R^1 = Ac; X = O



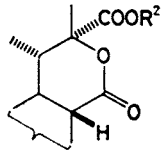
IX, R^1 = R^2 = R^3 = H
X, R^1 = Ac; R^2 = H; R^3 = CH_3
XI, R^1 = Ac; R^2 = R^3 = H



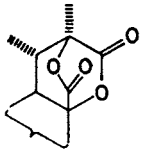
XII, R^1 = Ac; R^2 = H
XIII, R^1 = Ac; R^2 = CH_3



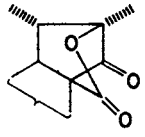
XIV, R^1 = R^2 = H
XV, R^1 = H; R^2 = CH_3
XVI, R^1 = Ac; R^2 = H
XVII, R^1 = Ac; R^2 = CH_3



XVIII, R^1 = R^2 = H
XIX, R^1 = H; R^2 = CH_3
XX, R^1 = Ac; R^2 = H
XXI, R^1 = Ac; R^2 = CH_3



XXII, R^1 = Ac



XXIII, R^1 = Ac

cleavage of the known[3] derivative *XXIII*. The acid *XIV* (or *XVI*) was obtained as the sole isomer only in the absence of alkali. It is therefore probable that this isomer retains the original *cis*-fusion of the lactone ring and the ring D (configuration 17α*H*) whereas in the isomeric compounds *XVIII*–*XXI* these rings are fused in a *trans*-manner (configuration 17β*H*).

This configurational assignment in position 17 was confirmed by ^{1}H NMR spectra

of acetates *XVII* and *XXI*. In the spectrum of *XVII*, the 17α*H* signal appears at δ 2·62 as a doublet of doublets of doublets with coupling constants 7·1, 4·8, and 1·7 Hz which – assuming slightly deformed chair forms of rings D and E – correspond to an equatorial hydrogen atom coupled with two axial (18α, 16α) and one equatorial (16β) hydrogen atoms. The signal of 19β-H (doublet of quartets at δ 1·85) exhibits coupling with the 18α-proton (J = 4·6 Hz), compatible with diequatorial arrangement of these protons in the *cis*-annelated rings D and E. Moreover, one of the methyl proton signals is shifted from the usual region of about δ 0·95–1·00 (see ref.*6*) to δ 0·80–0·85. Apparently, this signal belongs to the 8β-methyl group, shielded with lactone carbonyl group, which in the 17α*H*-isomer *XVII* is axial (relative to the D-ring). On the other hand, no such shielding of the 8β-methyl group occurs in the *trans*-annelated 17β*H*-isomer *XXI* and the signal of the axial 17β-proton (δ 2·25) shows two high coupling constants (12·5 and 10·5 Hz) due to coupling with the axial protons in positions 16α and 18α.

The acid *XVI* of 17α*H*-configuration was also obtained by thermal decarboxylation of diacid *XII* at 290–300°C, along with dilactone *XXII* and norketolactone *XXIII*. The structure of the latter two compounds has been unequivocally confirmed[3] *inter alia* by oxidation of hydroxy acid *XI* with lead tetraacetate to *XXIII* and its conversion into dilactone *XXII* by treatment with 3-chloroperoxybenzoic acid. When diacid *XII* was pyrolyzed at 300–310°C, compounds *XXII* and *XXIII* were obtained as the sole reaction products. The acid *XVI* is undoubtedly an intermediate since on heating to 290–310°C it decomposed to a 1 : 1 mixture of *XXII* and *XXIII*. These unusual pyrolytic reactions formally correspond to elimination of water (formation of *XXIII*) or elimination of two hydrogen atoms (formation of *XXII*) from acid *XVI*. The second reaction pathway would involve oxidation with air oxygen and base-catalysis with glass. Such assumptions are supported by the following observations. On heating on a Kofler block (on a microscope glass), acid *XVI* melted with decomposition at 290–295°C to give *XXII* and *XXIII*, whereas on a platinum foil it did not melt and remained unchanged (TLC) even at 320°C. However, addition of glass powder again led to decomposition to *XXII* and *XXIII* at 290–300°C. When the pyrolysis was carried out in a glass vessel under argon at 305–315°C, a mixture of many compounds was obtained, containing (according to TLC) only traces of *XXIII* and no *XXII*. Contrary to acid *XVI*, heating the isomeric 17β*H*-acid *XX* to 300°C afforded neither *XXII* nor *XXIII*.Obviously formation of these compounds from acid *XVI* requires *cis*-arrangement of the carboxyl group on C(20) and the hydrogen atom on C(17).

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Specific rotations were measured in chloroform (*c* 0·2–0·7) on an automatic polarimeter ETL-NPL (Bendix–Ericson), accuracy ±2°. Infrared spectra were taken in chloroform on a UR-20 (Zeiss, Jena) spectrometer.

Proton NMR spectra were measured on Tesla BS-487 A (80 MHz) or (where stated) on Varian XL-200 (200 MHz) spectrometers in deuteriochloroform with tetramethylsilane as internal standard; chemical shifts are given in ppm (δ-scale). Mass spectra were obtained with a Varian MAT-311 instrument, energy of ionizing electrons 70 eV, ionizing current 1 mA, ion source temperature 200°C, direct inlet at 130–200°C. Analytical as well as preparative thin-layer chromatography (TLC) was performed on silica gel G according to Stahl (Merck). Column chromatography was carried out on silica gel according to Pitra (30–60 μm). Acetates were prepared by treatment with a 1 : 1 mixture of pyridine and acetic anhydride at room temperature for 12 h. Methyl esters were obtained by reaction with diazomethane in ether. The identity of compounds was checked by their melting points, optical rotations, IR spectra, and TLC.

3β-Acetoxy-22-hydroxymethylene-21-oxo-18α,19β*H*-ursan-28→20β-olide (*VII*)

A suspension of *IV* (0·36 g) in benzene (50 ml) and ethyl formate (5·5 ml) was added dropwise at 15–18°C to a stirred suspension of sodium hydride (0·4 g) in benzene (10 ml). After stirring at room temperature for 15 h, the mixture was decomposed with 2% hydrochloric acid (100 ml), the benzene layer was separated and the aqueous one washed with chloroform. The combined organic phases were washed with water, dried over sodium sulfate and taken down. Crystallization of the residue (0·36 g) from methanol and chloroform–heptane afforded 3β-hydroxy-22-hydroxymethylene-21-oxo-18α,19β*H*-ursan-28→20β-olide (*V*), m.p. 306–312°C (decomp.); $[\alpha]_D$ +46°. IR spectrum: 3 620, 1 765, 1 680, 1 605 cm^{-1}. For $C_{31}H_{46}O_5$ (498·7) calculated: 74·66% C, 9·30% H; found: 74·44% C, 9·47% H.

Diacetate VI: m.p. 250–260°C (decomp.) (chloroform–heptane), $[\alpha]_D$ +57°. IR spectrum: 1 790, 1 765, 1 730, 1 640, 1 260 cm^{-1}. For $C_{35}H_{50}O_7$ (582·8) calculated: 72·13% C, 8·68% H; found: 71·89% C, 8·48% H.

Monoacetate VII: A solution of *VI* (0·1 g) in acetone (17 ml) containing 10% hydrochloric acid (3 drops) was set aside at room temperature for 17 h. The solvent was removed under diminished pressure and the residue washed with methanol. Crystallization from chloroform–methanol and chloroform–heptane gave *VII*, m.p. 305–315°C (decomp.); $[\alpha]_D$ +55°. IR spectrum: 1 765, 1 730, 1 680, 1 610, 1 260 cm^{-1}. For $C_{33}H_{48}O_6$ (540·7) calculated: 73·30% C, 8·95% H; found: 72·95% C, 8·92% H.

3β-Acetoxy-21,22-dioxo-18α,19β*H*-ursan-28→20β-olide (*VIII*)

A suspension of *IV* (0·5 g) and selenium dioxide (0·5 g) in a mixture of acetic acid and dioxane (1 : 1; 30 ml) was refluxed for 8 h. The mixture was concentrated, the residue diluted with water and the separated product (0·5 g) filtered and chromatographed on silica gel. Two unidentified compounds were eluted first: The first (0·08 g) melted at 330–336°C (decomp.), $[\alpha]_D$ +3°, IR spectrum: 3 500 (broad), 1 762, 1 723, 1 250 cm^{-1}; the second (0·1 g) had m.p. 319–321°C (decomp.) (chloroform–heptane), $[\alpha]_D$ +18°, IR spectrum: 3 500 (broad), 1 763, 1 719, 1 256 cm^{-1}. The product *VIII* (0·3 g) was eluted as the most polar component; m.p. 305–310°C (decomp.) (chloroform–heptane), $[\alpha]_D$ +72°. IR spectrum: 1 785, 1 750, 1 735, 1 260 cm^{-1}. ^1H NMR spectrum: 0·85 s (3 × CH_3), 0·89 s (CH_3), 0·98 s (CH_3), 1·54 s (CH_3), 0·93 d (CH_3-19α, $J = 7$), 2·03 s ($OCOCH_3$), 4·47 m (H-3α). For $C_{32}H_{46}O_6$ (526·7) calculated: 72·97% C, 8·80% H; found: 72·62% C, 8·57% H.

3β-Acetoxy-20β,28-epoxy-18α,19β*H*-ursane-21,22-dione (*II*)

Using the procedure described for *VIII*, compound *I* (0·2 g) was converted into the title com-

pound (0·19 g), m.p. 328—330°C (chloroform–heptane), $[\alpha]_D$ +96°. IR spectrum: 1 755, 1 731, 1 255 cm^{-1}. ^1H NMR spectrum: 0·84 s (2 × CH_3), 0·88 s (2 × CH_3), 1·03 s (CH_3), 1·25 s (CH_3), 2·03 s ($OCOCH_3$), 4·86 d and 4·49 d (H_2-28, J = 10), 4·46 m (H-3α). Doublet of CH_3-19α is overlapped by other methyl signals. For $C_{32}H_{48}O_5$ (512·7) calculated: 74·96% C, 9·44% H; found: 74·79% C, 9·35% H.

Benzilic Rearrangement of α-Diketones *II* and *VIII*

A) A solution of *II* (50 mg) and potassium hydroxide (0·2 g) in a mixture of benzene and ethanol (1 : 1; 20 ml) was refluxed for 1 h. After cooling to room temperature, the mixture was diluted with water, acidified with 5% hydrochloric acid and extracted with ether. The ethereal layer was washed with water and the solvent was evaporated without drying. Crystallization from benzene–methanol afforded acid *III* (30 mg), m.p. 325—330°C (decomp.), identical with a sample obtained previously[1]. The identity was confirmed also by conversion into the known[1] diacetate.

B) Compound *VIII* (50 mg) was converted into acid *IX* (procedure *A*) and further into the diacetate (30 mg), m.p. 263—265°C (decomp.) (chloroform–heptane), $[\alpha]_D$ −86°, identical with a previously obtained[3] sample (reported[3] m.p. 265—267°C (decomp.), $[\alpha]_D$ −85°).

C) Sodium hydrogen carbonate (30 mg) was added to a solution of *VIII* (30 mg) in a mixture of chloroform and methanol (1 : 1; 2 ml). After standing at room temperature for 15 h, the mixture was filtered and the filtrate concentrated to crystallization. Yield 28 mg of ester *X*, m.p. 318—320°C, $[\alpha]_D$ −27°, identical with a sample obtained previously[3]. Erroneously reported[3] m.p. 287—290°C and $[\alpha]_D$ +34°.

Oxidation of Lactone *VIII*

A) Jones reagent was gradually added to a boiling solution of *VIII* (1·0 g) in chloroform (5 ml) and acetone (50 ml). After 2 h the excess reagent was reduced with methanol and the solvents were evaporated under diminished pressure. The residue was mixed with dilute hydrochloric acid and extracted alternately with ether and ethyl acetate. The combined organic phases were washed with water, dried over sodium sulfate and taken down. The residue was repeatedly extracted with boiling ether, leaving the diacid *XII* undissolved (0·25 g), m.p. 295—299°C (decomp.), $[\alpha]_D$ +4°. IR spectrum: broad band at about 3 000, 1 760, 1 730, 1 260 cm^{-1}. Mass spectrum, m/z (%): 516 (M^+ − 44; 2), 471 (3), 456 (19), 441 (12), 413 (30), 395 (6), 189 (65), 43 (100). For $C_{32}H_{48}O_8$ (560·7) calculated: 68·54% C, 8·63% H; found: 68·76% C, 8·75% H.

Dimethyl ester XIII: m.p. 302—305°C (decomp.) (chloroform–light petroleum), $[\alpha]_D$ −5°. IR spectrum: 1 740, 1 723, 1 434, 1 260 cm^{-1}. Mass spectrum, m/z (%): 588 (M^+; 2), 529 (10), 528 (10), 513 (4), 485 (5), 469 (4), 189 (42), 43 (100). For $C_{34}H_{52}O_8$ (588·8) calculated: 69·36% C, 8·90% H; found: 69·35% C, 8·82% H.

The ethereal extract was taken down and chromatographed on silica gel. Elution afforded successively: *XXII* (0·08 g), not melting up to 360°C, identical with an authentic sample[3]; *XVI* (0·43 g), m.p. 295—300°C (decomp.) (chloroform–light petroleum), $[\alpha]_D$ +34°. IR spectrum: broad band at 3 000, 1 750 (sh), 1 725, 1 260 cm^{-1}. ^1H NMR spectrum: 0·84 s (3 × CH_3), 0·91 s (2 × CH_3), 1·00 d (CH_3-19, J = 7), 1·65 s (CH_3-20), 2·02 s ($OCOCH_3$), 2·69 m (H-17α, $W_{1/2}$ = 15), 4·44 m (H-3α). Mass spectrum; m/z (%): 516 (M^+; 0·5), 471 (1), 456 (6), 441 (3), 413 (6), 189 (15), 43 (100). For $C_{31}H_{48}O_6$ (516·7) calculated: 72·06% C, 9·36% H; found: 71·92% C, 9·20% H.

Methyl ester XVII: m.p. 280—283°C (ether–light petroleum), $[\alpha]_D$ +37°. IR spectrum: 1 737, (1 723 sh), 1 429, 1 258 cm^{-1}. ^1H NMR spectrum (200 MHz): 0·818 s (CH_3), 0·830 s (CH_3),

0·840 s (CH_3), 0·883 s (CH_3), 0·905 s (CH_3), 1·238 d (CH_3-19, J = 7·2), 1·598 s (CH_3-20), 1·85 dq (H-19β, J(18,19) = 4·6; J(19, 29) = 7·2), 2·03 s ($OCOCH_3$), 2·62 ddd (H-17α, J = 7·1, 4·8, and 1·7), 3·73 s (OCH_3), 4·46 m (H-3α). Mass spectrum, m/z (%): 530 (M^+; 23), 471 (23), 470 (36), 455 (18), 427 (38), 388 (8), 189 (54), 43 (100). For $C_{32}H_{50}O_6$ (530·7) calculated: 72·42% C, 9·50% H; found: 72·56% C, 9·63% H. The last fraction contained another portion of *XII* (0·1 g).

B) A mixture of *VIII* (0·1 g), chloroform (2 ml), and 30% aqueous peroxyacetic acid (2 ml) was allowed to stand at room temperature for 4 h with intermittent shaking. After pouring into water, the product was extracted with ether and the ethereal extract was washed successively with water, solutions of potassium iodide and sodium pyrosulfite, again with water, and dried over sodium sulfate. The solvent was evaporated and the residue (0·1 g) treated with ethereal diazomethane. Crystallization from chloroform–light petroleum gave *XIII* (0·08 g), identical with the product prepared under *A*).

Oxidation of Hydroxymethyleneketone *VII*

A mixture of *VII* (0·13 g) and chromium trioxide (0·5 g) in acetic acid (15 ml) was set aside for 40 min at room temperature. After reduction of excess oxidation reagent with methanol, the mixture was diluted with water and extracted alternatively with ether and ethyl acetate. The combined extracts were washed with water, dried over sodium sulfate, taken down and treated with a solution of diazomethane. Preparative TLC on silica gel in light petroleum–acetone (4 : 1) afforded: *XXII* (0·01 g), not melting up to 360°C, *XVII* (0·02 g), m.p. 273—276°C, and *XIII* (0·06 g), m.p. 303—306°C, all identical with the compounds described above.

Decarboxylation of Diacid *XII*

A) A mixture of *XII* (0·13 g), *p*-toluenesulfonic acid (20 mg), and acetic anhydride (5 ml) was refluxed for 30 min. After removal of acetic anhydride under diminished pressure, the residue was mixed with water (1 ml) and chloroform (10 ml) and briefly boiled. A part of the solvent was slowly distilled off and the residue was dried over sodium sulfate and filtered through a layer of silica gel. Crystallization from chloroform–heptane yielded 0·11 g of *XVI*, identical with an authentic sample.

B) A solution of *XII* (0·25 g) and potassium hydroxide (0·6 g) in benzene–ethanol (1 : 1; 20 ml) was refluxed for 2 h. A part of the solvents was distilled off and the residue mixed with dilute hydrochloric acid. The precipitate was collected, washed with water, dried and repeatedly extracted with boiling acetone. The insoluble material consisted of the acid *XVIII* (0·11 g), m.p. 298—302°C (decomp.). Mass spectrum, m/z (%): 474 (M^+, 6), 456 (30), 441 (29), 413 (42), 395 (16), 207 (62), 189 (100). For $C_{29}H_{46}O_5$ (474·7) calculated: 73·38% C, 9·77% H; found: 73·04% C, 9·62% H.

Methyl ester XIX: 262—266°C (decomp.) (chloroform–heptane), $[\alpha]_D$ +41·5°. IR spectrum: 3 608, 1 737, 1 433 cm^{-1}. Mass spectrum, m/z (%): 488 (M^+, 12), 486 (5), 470 (97), 455 (55), 429 (49), 427 (39), 207 (60), 189 (100). For $C_{30}H_{48}O_5$ (488·7) calculated: 73·73% C, 9·90% H; found: 73·56% C, 9·86% H.

3-*Acetate* XX: decomposition above 300°C (chloroform–heptane). Mass spectrum (inlet system temperature 260°C), m/z (%): 472 (M^+ — 44; 3), 442 (8), 412 (23), 397 (23), 395 (17), 189 (100). For $C_{31}H_{48}O_6$ (516·7) calculated: 72·06% C, 9·36% H; found: 72·42% C, 9·37% H.

Methyl ester-3-*acetate* XXI: m.p. 245—250°C (decomp.) (chloroform–heptane), $[\alpha]_D$ +43°. IR spectrum: 1 728, 1 435, 1 256 cm^{-1}. ^1H NMR spectrum (200 MHz): 0·848 s (CH_3), 0·858 s

(CH_3), 0·888 s (CH_3), 0·918 s (CH_3), 1·003 s (CH_3), 0·908 d (CH_3-19, J = 7·2), 1·770 s (CH_3-20), 2·05 s ($OCOCH_3$), 2·25 bdd (H-17β, J = 10·5 and 12·5), 3·79 s (OCH_3), 4·48 m (H-3α). Mass spectrum, m/z (%): 530 (M^+, 2·5), 515 (1), 470 (47), 455 (22), 427 (16), 395 (4), 388 (3), 189 (100), 43 (83). For $C_{32}H_{50}O_6$ (530·7) calculated: 72·41% C, 9·50% H; found: 72·54% C, 9·49% H.

The acetone extract, obtained under *B*), was taken down and the residue (0·11 g) was subjected to TLC on silica gel in light petroleum–ether–acetone (3 : 3 : 1). The chromatography gave (along with 35 mg of acid *XVIII*) the acid *XIV* (70 mg); m.p. 290—295°C (decomp.) (acetone). Mass spectrum, m/z (%): 474 (M^+, 1) 456 (11), 441 (9), 413 (12·5), 395 (2), 207 (71), 189 (100). For $C_{29}H_{46}O_5$ (474·7) calculated: 73·38% C, 9·77% H; found: 72·99% C, 9·65% H.

Methyl ester XV: m.p. 280—285°C (decomp.) (chloroform–heptane), $[\alpha]_D$ +34°. IR spectrum: 3 610, 1 737, 1 435 cm^{-1}. Mass spectrum, m/z (%): 488 (M^+, 21), 486 (14), 470 (33), 455 (45), 427 (40), 411 (16), 401 (35), 388 (42), 207 (79), 189 (100). For $C_{30}H_{48}O_5$ (488·7) calculated: 73·73% C, 9·90% H; found: 72·95% C, 9·84% H.

Isomerization of Methyl Esters *XVII* and *XXI*

Ester *XVII* or *XXI* (50 mg) was refluxed with 2·5% solution of potassium hydroxide in benzene–ethanol (1 : 1; 3 ml) for 2 h. The mixture was diluted with water, acidified with dilute hydrochloric acid and extracted alternately with ether and ethyl acetate. The combined organic extracts were washed with water, dried over sodium sulfate and taken down. After acetylation and reaction with diazomethane, the products were separated by TLC on silica gel in light petroleum–chloroform–acetone (5 : 1 : 1). The obtained *XVII* (12 and 10 mg, respectively) and *XXI* (30 and 28 mg, respectively) were identical with authetic samples.

Alkaline Cleavage of *XXIII*

A solution of *XXIII* (0·17 g) and potassium hydroxide (1·5 g) in benzene–ethanol (1 : 1; 30 ml) was refluxed for 2 h, the mixture was concentrated under diminished pressure and processed as in the preceding experiment. Reaction with diazomethane, acetylation and separation by TLC on silica gel afforded *XVII* (30 mg), m.p. 273—276°C, and *XXI* (90 mg), m.p. 251—254°C, both identical with the above-prepared samples.

Pyrolysis of Acids *XII* and *XVI*

A) Diacid *XII* was heated to 295—300°C for 2 min on a Kofler block. After reaction with ethereal solution of diazomethane, the mixture contained four products, identified by TLC on silica gel as *XIII*, *XVII*, *XXII*, and *XXIII*.

B) Acid *XVI* (30 mg) was heated on a Kofler block to 290—305°C for 7 min and the mixture was separated by preparative TLC on silica gel in light petroleum–ether (1 : 1) to give 10 mg of *XXII*, not melting up to 360°C, $[\alpha]_D$ +41° (reported[3]: not melting up to 360°C, $[\alpha]_D$ +40°), and 12 mg of *XXIII*, m.p. 339—341°C, $[\alpha]_D$ +16° (reported[3] m.p. 336—338°C, $[\alpha]_D$ +18°). Both products were identical with samples prepared previously[3].

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