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SYNTHESIS OF TWO STEREOISOMERS OF (±)-9-DESOXOCASSAMIC ACID

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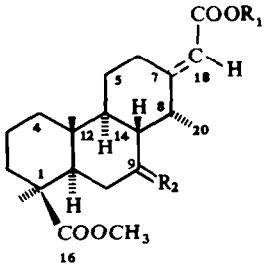
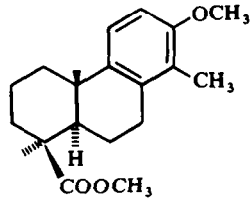
Abstract—The synthesis of the epimers of (±)-9-desoxocassamic acid (I) (at C-8 and at C-14) is described. The catalytic hydrogenation of the aromatic ring of methyl(±)-7-hydroxy-8-methyldesoxypodocarpate (VIII) to give the thermodynamically stable methyl(±)-7-oxo-8β-methylpodocarpan-16-oate (VII) and methyl(±)-7-oxo-8α-methyl-11α, 12β, 13α, 14α-podocarpan-16-oate (XI) is discussed. A new sterioisomer of (±)-9-desoxodihydrocassamic acid is described.

(±)-9-DESOXOCASSAMIC acid (I) is a typical tricyclic diterpene with the cassane skeleton obtained "via" acid hydrolysis of the alkaloid cassamina (II) followed by reduction of (±) cassamic acid (III) at C-9.[1]



I: $R_1 = H$ $R_2 = H_2$
II: $R_1 = (CH_2)_2N(CH_3)$, $R_2 = 0$
III: $R_1 = H$ $R_2 = 0$



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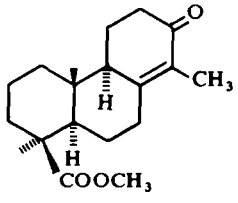

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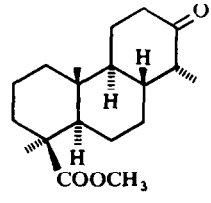

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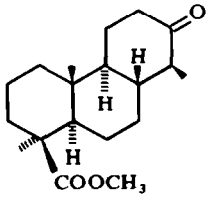
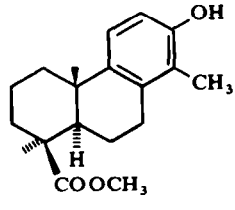


VII



VIII

In previous papers,[2] the preparation of methyl (±)-7-methoxy-8-methyldesoxypodocarpate (IV)* and methyl (±)-7-oxo-8-methylpodocarp-8-en-16-oate (V) has been described, and their stereochemistry determined with the synthesis of acid I in mind. While we were able to obtain the methoxy ester (IV) with high over-all yield, the α-β unsaturated ketone (V) was obtained from IV by Birch reduction (with difficulty and in poor yield). The final approach to the acid I was based on the sequence V → VI → I. Unfortunately, the last phase has offered some surprises concerning the programmed synthetic route. The results obtained are the subject of this paper.

In connection with our initial purpose, the α-β unsaturated ketone (V) was hydrogenated over 10% Pd-C in acetic acid under 60 atm hydrogen pressure at room temperature. Jones oxidation of the resulting alcoholic material gave a ketonic mixture. The only product we were able to isolate, in pure form, by column and TLC, was the methyl (±)-7-oxo-8β-methylpodocarpan-16-oate (VII). This ketone was recovered unchanged by treating with methanolic sodium methoxide or with mineral acids. The stereochemistry of the ketone (VII) was proven by direct comparison (mixture m.p. and IR) with an authentic sample.[3]

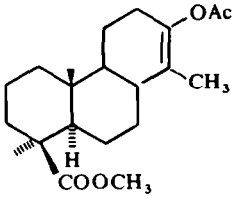
Since the Birch reduction of methoxy ester IV gives the α-β unsaturated ketone (V) in poor yield,[2b] and the reduction of this affords the ketone VII with undesired stereochemistry at C-8, we directed our attention to the catalytic reduction of the aromatic ring. To this end the phenol (VIII) was prepared in 73% yield from the methoxy ester (IV) by treatment with hydrobromic-hydriodic acid in glacial acetic acid and final re-esterification with diazomethane. The crystalline phenol (VIII) was then subjected, in alkaline medium, to high-pressure hydrogenation in the presence of Raney Ni, and the resulting stereoisomeric mixture of saturated hydroxy esters† was oxidized directly with Jones reagent. The ketonic material obtained was chromatographed on alumina and the TLC on silica gel showed that two products were present, in an approximate ratio of 1:1. The ketonic mixture was then patiently separated (Experimental) and the structures of resulting two ketones (m.p. 119° and m.p. 130°) were investigated.

The compound melting at 130° was identified as the ketone VII by direct comparison (mixed m.p. and IR). The ketone, m.p. 119°, was converted into the 7(8)-enol acetate (IX) in acetic anhydride-carbon tetrachloride-perchloric acid.[4] Bromination of IX in collidine-acetic acid gave the 8-bromo-ketone (X) which was dehydrobrominated to give the known α-β unsaturated ketone (V).[2b] The sequence IX → X → V shows, therefore, that the 119° ketone is a stereoisomer of VII. The stereochemistry at C-8 and C-14 has not yet been determined. Four structures are possible in theory: VI, VII, XI and XII. The first and the fourth must be rejected because (in this case) the compound would have undergone epimerization at C-8 giving the thermodynamically stable epimer (VII or XI). However equilibration with methanolic sodium methoxide or with mineral acids gave the unchanged starting ketone. The second structure obviously may be eliminated and therefore the stereochemistry of the 119° ketone implies a *trans*-anti-*cis* arrangement with 20-Me α-equatorial as depicted in XI.‡

* The nomenclature used is that of W. Klyne, *J. Chem. Soc.* 3072 (1953). The formulae depicted always represent a racemate unless otherwise specified.

† The ester group of VIII is only slightly hydrolyzed (Experimental), in agreement with its axial nature.

‡ We have assumed that ring B adopts a normal chair conformation.[5] A compound with a *trans-anti-cis* configuration possessing ring B in a boat form is ruled out by a large interaction which would be introduced.[6] A distorsion of ring C from the normal chair conformation is possible.[6a-7]



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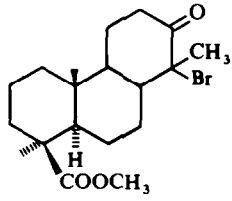
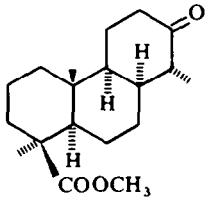
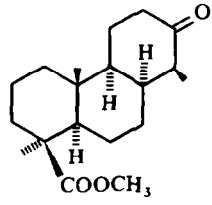


X



XI



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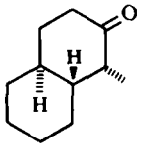

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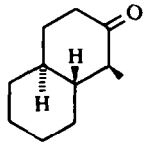

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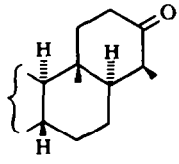

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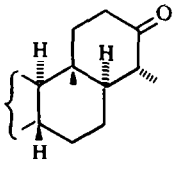
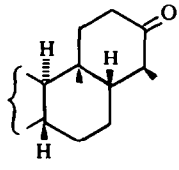


XVI



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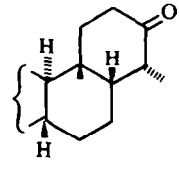

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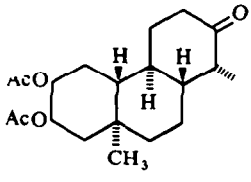

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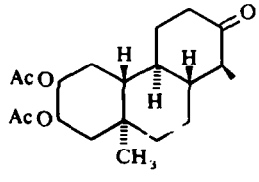
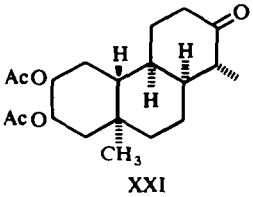
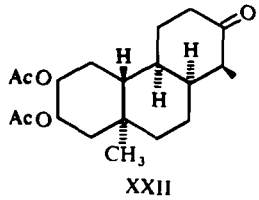


XX

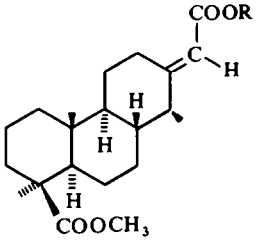


XXI

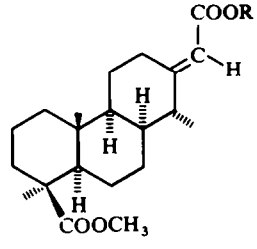


XXII

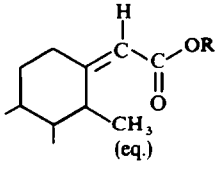
The correlation between the stability of tricyclic ketones (VII and XI) under enolizing conditions and their stereochemistry at C-8 is firmly based. Indeed Turner *et al.*[8] have reported that the ketone XIII is quantitatively converted into XIV on treatment with base. However, the ketone XIV was recovered unchanged when was exposed for prolonged periods to the action of sodium methoxide in methanol. The conclusion is, therefore, that the equatorial arrangement of the Me group in XIV is thermodynamically preferred to the alternate, axial, arrangement. Similarly Mazur,[9] and Turner,[8] were able to prove that the 4β-methylcholestan-3-one (XV) is smoothly isomerized by sulphuric acid or by sodium methoxide into the 4α-methylcholestan-3-one (XVI). The stereoisomer 4β-methylcoprostan-3-one (XVII), however, could not be epimerized and the Me group is therefore assigned as β equatorial. A tricyclic ketone which possesses the perhydrophenanthrene arrangement has been reported by Woodward *et al.*[10] The ketone XIX was transformed, by treatment with base and reacetylation, into isomer XX, whereas XXI was recovered unchanged from such experiments. The ketones XVIII and XXII are regarded by the authors above cited[9,10] as molecules in which steric repulsions of the axial Me group "alpha" to the CO function are so great as to prevent their formation (by hydrogenation), or isolation, without epimerization. In the ketone XII the presence of 17-Me causes more severe steric repulsion and therefore its easy epimerization is a justified hypothesis.



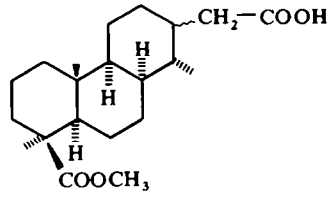
XXIII: R = C_2H_5
XXIV: R = H



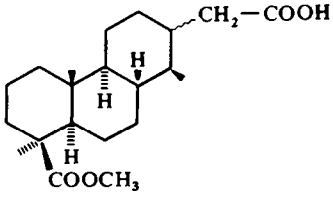
XXV: R = C_2H_5
XXVI: R = H



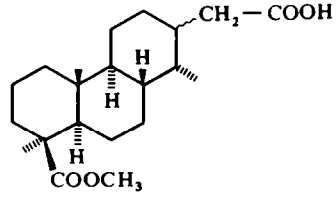
XXVII



XXVIII



XXIX



XXX

Considering these results, the isolation of the ketone VII from hydrogenation of V does not exclude that the saturation of double bond of V proceeds by "*cis*" addition of hydrogen at C-8, because at present we cannot prove if the ketone VI is stable under the conditions used in the isolation of its epimer (VII). Since it was proven[9,10] that the ketones (XVI and XX) have been formed directly in the hydrogenation of the corresponding α-β unsaturated ketones, probably this occurs also for VII. We do not know if the ketones (VII and XI) have been formed directly in the catalytic hydrogenation of VIII, or if some isomerization occurs at C-8 during their isolation (or at an intermediate stage in the hydrogenation process). However, the backbone arrangement *trans-anti-trans* in VII and *trans-anti-cis* in XI exclude the *cis*-hydrogenation as the sole process. In the formation of XI it is, indeed, possible that all hydrogens are introduced from the same side, to give, initially, the thermodinamically unstable XII, but the ketone VII is a product of *trans*-addition of hydrogen. This requires that the hydrogenation of the ring does not occur only during single stage adsorption on the catalyst, but that multiadsorption processes are also involved. There are many cases in the literature of this phenomenon.[11,*]

In our synthetic attempt, the ketones (VI and XI) were treated with ethoxyethyne[13] "via" a Grignard reaction and the corresponding ethoxyethynylcarbinols were isomerized in the presence of dilute acid to give the ethyl esters, (XXIII and XXV) respectively. Alkaline hydrolysis of XXIII and XXV afforded, as the sole isolable products, the crystalline C-8-epimer of (±)-9-desoxocassamic acid (XXIV) and C-14-epimer of (±)-9-desoxocassamic acid (XXVI). Though an excess of ethoxyethynyl magnesium bromide was used, an amount of the starting ketone (VII or XI respectively) was recovered. The acid XXIV has an identical IR spectrum with that of an authentic sample,[3] and therefore the stereochemistry at C-18 (carboxyl group *trans*) of this compound is defined.

The proven *trans*-isomerism of the acid (XXIV), the isolation of a sole isomer from the condensation reaction and the recovery of the unchanged starting ketone, can be regarded as evidence that the equatorial 20-Me controlled the steric course of the olefin synthesis.[1c] Indeed, the *cis* isomer (see partial structure XXVII) would possess severe non-bonded interactions between the equatorial Me group and the CO group of the ester.[14] Similar stereochemical results are also to be expected for the ketone XI which has the 20-Me in the equatorial (α) configuration. The corresponding acid is therefore a *trans* isomer as depicted in the formula XXVI. The IR spectra of the acids (XXIV and XXVI) are similar, but significant differences are present in the 1100–1300 cm^{-1} region.

Catalytic hydrogenation of XXVI over Adams' platinum oxide in ethanol [the same catalyst and solvent as used for the hydrogenation of (−)-9-desoxocassamic acid (I)[1b]] gives the crystalline acid XXVIII. The IR spectrum of XXVIII is similar to the optically active desoxodihydro cassamic acid (XXX)[1b] and XXIX obtained by reduction[3] of XXIV, but significant differences are present for all three compounds in the 1100–1160 cm^{-1} and 1300–1400 cm^{-1} regions.

* The results of the present work induce us to re-examine the results obtained previously[12] in the catalytic hydrogenation of analogous compounds.

EXPERIMENTAL

All m.ps are uncorrected IR spectra were recorded on a Perkin–Elmer IR spectrophotometer mod. 357. For chromatography neutral alumina (C. Erba) and silica gel PF_{254} (Merck) were used. Pet ether refers to the fraction b.p. 40–60°.

Catalytic hydrogenation of α-β *unsaturated ketone* (V)

The ketone V (100 mg) was dissolved in AcOH (80 ml) and hydrogenated in the presence of 10% Pd-C for 4 hr at 60 atm and room temp. The catalyst was removed by filtration, and the Ac OH was then evaporated under reduced press. The residue was worked up in the usual way and then oxidized with Jones reagent. The product was then isolated by the usual procedure, chromatographed on alumina, purified by TLC and, after crystallization from EtOAc, furnished 35 mg of VII m.p. 127–129°. The IR spectra were identical and no depression in m.p. was observed on admixture with an authentic sample.[3]

Methyl(±*)-7-hydroxy-8-methyldesoxypodocarpate* (VIII)

The ester IV (5 g) in AcOH (85 ml) was mixed with 48% HBr (56 ml) and 57% HI (14 g). After refluxing for 8 hr, the mixture was diluted with water and the crystalline phenolic acid was filtered off and washed with water. The crude acid (4·2 g) was then treated with the ethereal diazomethane to give 3·5 g (73%) of VIII which recrystallized from EtOAc, m.p. 203–204°; ν_{max} (Nujol) 3380, 1718, 1690, 1595, 1150, 810 cm^{-1}. The indentity of VIII was proven by IR and m.m.p. comparison.[2a]

Catalytic hydrogenation of methyl(±*)-7-hydroxy-8-methyldesoxypodocarpate* (VIII)

A soln of VIII (4·6 g) in 95% EtOH (322 ml) containing 23% KOH aq (10 ml) was hydrogenated over Raney Ni (74 g) at 160–165° and an initial press of 140 Kg/cm^2 for 10 hr. The catalyst was filtered off and the filtrate concentrated *in vacuo*. The residue was diluted with water and extracted with ether. After washing and drying over Na_2SO_4 the ether was removed by evaporation to give 3·7 g of partly crystalline material. The crude reduction mixture in acetone (150 ml) was oxidized directly with the Jones reagent (3·5 ml) at 2–5°. The soln was then allowed to stand at 5° for 30 min. The excess reagent was decomposed by MeOH and the mixture concentrated *in vacuo*. The residue was extracted with ether and, after washing and drying, the solvent was evaporated. The crude semisolid material obtained in this way was purified by chromatography on alumina by eluting with benzene. An oil and a crystalline mixture (2 g, m.p. 105–118s) of VII and XI were isolated. The ketones VII and XI were then separated as reported below.

The above alkaline layer from etheral extraction was acidified and extracted with ether. The crude material obtained was esterified and oxidized with Jones reagent to afford an additional 0·1 g of the mixture of VII and XI.

Methyl(±*)-7-oxo-8*β*-methylpodocarpan-16-oate* (VII) *and methyl(*±*)-7-oxo-8*α*-methyl-11*α*, 12*β*, 13*α*, 14*α*-podocarpan-16-oate* (XI)

The mixture of VII and XI (2·1 g) was crystallized from EtOAc at room temp. The crystalline ppt was recrystallized from the same solvent to give XI (0·420 g), m.p. 118–119°; ν_{max} (Nujol) 1725, 1713, 1240, 1170 cm^{-1}. (Found: C, 74·49; H, 9·83. $C_{19}H_{30}O_3$ requires: C, 74·46; H, 9·88%); 2,4-dinitrophenyl-hydrazone m.p. 230–231° from EtoAc, (Found: C, 61·83; H, 7·08; N, 11·53. $C_{25}H_{34}O_6N_4$ requires: C, 61·71; H, 7·05; N, 11·51%). The combined mother liquors were evaporated and the residual mixture of VII and XI was chromatographed on eighty silica gel coated plates (20 × 20 cm) having a 0·3 mm coating. The developing solvent was benzene-ether (9 :1) or cyclohexane ethyl acetate (9 :1). By treating a small portion of the coated plates with the aerosol of ethanolic acid soln of 2,4-dinitrophenylhydrazine, the resulting two bands were visualised. The band, R_f about 0·5, was marked, scraped off and eluted with ether to give (0·120 g) of XI. The band R_f about 0·6, was worked up in the usual way, afforded (0·480 g) of VII m.p. 128–130° from EtOAc; ν_{max} (Nujol) 1728, 1712, 1230, 1163 cm^{-1}. (Found: C, 74·51; H, 9·91. $C_{19}H_{30}O_3$ requires: C, 74·46; H, 9·88%); 2,4-dinitrophenylhydrazone m.p. 219–220° from EtOAc, (Found: C, 61·87; H, 7·02; N, 11·49. $C_{25}H_{34}O_6N_4$ requires: C, 61·71; H, 7·05; N, 11·51%). The compound VII was identical (m.m.p. and IR) with a sample obtained from hydrogenation of V.

Attempted epimerization at C-8 *of the keto ester* VII

(a) A soln of VII (20 mg) and NaOMe (from 50 mg Na) in MeOH (5 ml), was refluxed for 2 hr. The product (15 mg) was isolated by a standard procedure. The material was identical in all respects with VII.

(b) The ketone VII (20 mg) in MeOH (5 ml) was refluxed with 1% HClaq (2 ml) for 1 hr. The starting ketone (16 mg) was recovered unchanged.

Attempted epimerization at C-8 *of the keto ester* XI

(a) The ketone XI (100 mg) in methanolic NaOMe soln was treated in the manner described for VII. The starting ketone (88 mg) was recovered unchanged. Identical results were obtained allowing the reaction mixture to stand at room temp for 48 hr.

(b) The ketone XI was also recovered unchanged by acid catalyzed epimerization, according to the procedure described above for VII.

Methyl(±)-7-*oxo*-8-*methylpodocarp*-8-*en*-16-*oate* (V)

A soln of XI (300 mg) in CCl_4 (3·1 ml) was treated with Ac_2O (0·16 ml) and 60% aqueous perchloric acid (0·01 ml) and kept at room temp for 24 hr. The mixture was diluted with ether and then washed with $NaHCO_3$ aq and brine. After drying (Na_2SO_4) the solvent was evaporated to give a residual oil (400 mg) [ν_{max} (film) 1755, 1725, 1212, 1155 cm^{-1}]. The crude IX was then dissolved in 1:10 v/v collidine-AcOH (6 ml) and treated with 1:10 v/v Br–AcOH soln (1·2 ml) under N_2. The mixture was kept in the dark at room temp for 24 hr. $NaHSO_3$aq was added and the product was isolated with ether in the usual way. The residue was adsorbed on alumina (20 g) and eluted with ether. The bromo ketone (220 mg) [ν_{max} (film) 1722, 1705, 1155 cm^{-1}] was not further purified. A soln of X (220 mg) in dimethylformamide (12 ml) was heated under reflux for 2 hr with sym-collidine (2 ml). After cooling, the mixture was diluted with ether washed with dil HCl, $NaHCO_3$aq and dried (Na_2SO_4). The solvent was evaporated *in vacuo* and the residual oil was chromatographed on alumina to give V (25 mg) m.p. 112–113°, identical (m.m.p., IR spectrum and its 2,4-dinitrophenylhydrazone) with an authentic sample.[2b]

C-14 *Epimer of* (±)-9-*desoxocassamic acid* (XXVI)

To a soln of EtMgBr [prepared from Mg (49 mg) and EtBr (245 mg)] in 5 ml dry ether was added over, a 5 min period at room temp under N_2, a soln of ethoxyethyne (156 mg) in dry ether (1 ml). The reaction mixture was allowed to stand at room temp for 1 hr and then heated under reflux for 15–20 min. After cooling, a soln of XI (400 mg) in dry ether (30 ml) was added and the mixture heated under reflux for 2 hr. The complex was decomposed with NH_4Claq and the product isolated by ether extraction. The residue obtained after removal of the ether was dissolved in MeOH (15 ml) and 10% H_2SO_4 (10 drops) was added. After 30 min at room temp under stirring, the mixture was diluted with water and extracted with ether. The extract was washed with water, dried (Na_2SO_4) and evaporated *in vacuo*. The resulting solid residue was dissolved in MeOH (10 ml) and NaOH (900 mg) in water (1 ml) was added. The mixture was refluxed for 3 hr, then the MeOH was removed *in vacuo* and the residue diluted with water. The aqueous soln was extracted with ether and the organic layer worked up as usual, affording XI (58 mg). The aqueous layer was acidified with dil HCl, and extracted with ether. The extract was washed with water then with sat NaClaq, dried (Na_2SO_4) and evaporated. Crystallization of the resulting solid from EtOAc afforded 85 mg of XXVI m.p. 188–190°, ν_{max} (Nujol) 1728, 1683, 1638, 1260, 1235, 1208, 1150, 878 $cm.^{-1}$ ν_{max} (CCl_4) 1728, 1688, 1640, 1250, 1230, 1205, 1148, 872 $cm.^{-1}$ (Found: C, 72·50; H, 9·31. $C_{21}H_{32}O_4$ requires: C, 72·37; H, 9·26%).

C-8 *Epimer of* (±)-9-*desoxocassamic acid* (XXIV)

The ketone VII (100 mg) was condensed with ethoxyethyne and hydrolyzed to give XXIV (18 mg), following the above procedure for the preparation of XXVI. The analytical sample, m.p. 217–218° (reported[3] m.p. 199–200°) was obtained after crystallization from EtOAc; ν_{max} (Nujol) 1722, 1684, 1628, 1270, 1233, 1222, 1160, 1153, 885 cm^{-1}; ν_{max} ($CHCl_3$) 1728, 1680, 1637, 1270, 1225, 1152, 881 cm^{-1}. The IR spectrum of XXIV was superimposable with that of an authentic sample.[3] (Found: C, 72·46; H, 9·30. $C_{21}H_{32}O_4$ requires: C, 72·37; H, 9·26%).

Catalytic reduction of XXVI

A soln of XXVI (43 mg) in 99% EtOH (10 ml) was hydrogenated for 3 hr over Adams' PtO_2 (43 mg) at room temp under atm press. After removal of the catalyst by filtration and the EtOH by distillation at reduced press, the residue was crystallized from EtOAc and afforded XXVIII (23 mg) m.p. 120–121°; ν_{max} (CCl_4) 1728, 1708, 1222, 1147 cm^{-1}. (Found: C, 71·73; H, 9·77. $C_{21}H_{34}O_4$ requires: C, 71·96; H,

9·79%). The IR spectrum of XXVIII is similar both to that of the optically active XXX and that of the racemic XXIX, but differences are present in the 1100–1160 cm^{-1} and 1300–1400 cm^{-1} regions.

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