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ISOLATION AND STRUCTURE OF JACQUINIC ACID[1]

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Abstract—Two triterpenes were isolated from the fruits of *Jacquinia pungens*. One of them was identified as *Primula genin A*. The other was shown to be 3β,16α,28-*trihydroxy-*β*-amyrin-*30β*-oic acid.*

Jacquinia pungens is a shrub which grows in the Isthmus of Tehuantepec (México). It is known as Palo de Niño or Sicqueté. As the crushed fruit is used for washing, the presence of saponins was suspected and for this reason an investigation was undertaken.

From the green fruit, after acid hydrolysis of the saponins, a triterpenoid sapogenin was isolated as the major product. The analysis indicated the empirical formula $C_{30}H_{50}O_3$ and the compound was identified as *primula genin A* (Ia)[2] by comparison with an authentic sample.[3]

From the acid fraction, a new triterpenoid acid was isolated as a major product. The analytical data indicated the empirical formula $C_{30}H_{48}O_5$. It was named *Jacquinic acid* (IIa) and was isolated as the main product from the mature fruits, together with a product whose analysis corresponds to the empirical formula $C_{32}H_{52}O_5$. The latter was shown to be the ethyl ester of jacquinic acid (IIc) since on saponification it gave jacquinic acid (IIa). Ethyl jacquinate (IIc) is, most probably, an artifact, formed during the acid hydrolysis of the fruit glycosides.

Jacquinic acid (IIa) readily gave a monomethyl ester (IIb), as shown by its analysis ($C_{31}H_{50}O_5$) and NMR data (one CO_2Me at 225 cps).[4]

Methyl and ethyl jacquinates gave an mild acetylation the respective diacetates (IId and IIe; $C_{35}H_{54}O_7$ and $C_{36}H_{56}O_7$) whose IR spectra still showed the presence of an hydroxyl group. Further acetylation, gave the corresponding triacetates (IIf and IIg; $C_{37}H_{56}O_8$ and $C_{38}H_{58}O_8$). Selenium dioxide oxidation of ethyl jacquinate triacetate (IIg) gave after saponification, the acid (VIII) whose UV absorption at 244, 252 and 261 mμ is characteristic of an heteroanular diene formed from β-amyrin triterpenes[5] by this type of oxidation.

Thus the functional groups of jacquinic acid were established as three hydroxyl groups and one carboxyl group on a β-amyrin system.

The abrupt change in triterpene composition between the green and the mature fruits, suggested a biogenetic and structural relationship between Primula genin A (Ia), isolated grom the green fruit and jacquinic acid (IIa), the only product found in the mature fruit.

[1] Contribution Nr. 177 from the Instituto de Química de la Universidad Nacional Autónoma de México.

[2] O. Jeger, C. Nisoli and L. Ruzicka, *Helv. Chim. Acta* **29**, 1183 (1946); B. Bischof and O. Jeger *Ibid* **31**, 1760 (1948).

[3] An authentic sample of *primula genin A* was kindly supplied by Prof. T. Reichstein.

[4] The NMR spectra were determined by Mr. Eduardo Díaz; on a Varian A-60 spectrometer, in $CDCl_3$, using tetramethylsilane as internal standard.

[5] L. Ruzicka and H. Schellenberg, *Helv. Chim. Acta* **22**, 767 (1939). D. H. R. Barton and C. J. W. Brooks, *J. Chem. Soc.* 257 (1951).

The correctness of this hypothesis was proved when jacquinic acid (IIa) was correlated with primula genin A (Ia).

For this purpose, jacquinic acid (IIa) was fully acetylated and transformed into the tritacetate acid chloride. Rosenmund reduction of the acid chloride afforded the aldehyde (IIIa), the NMR spectrum of which showed the characteristic signal due to the hydrogen of the aldehyde group at 572 c/s. Wolf-Kishner reduction of the aldehyde group, gave a triol which was identical in all respects to primula genin A (Ia). The position and stereochemistry of the three hydroxyl groups in this triterpene acid are fixed by the sequence of reactions so far described.[6]

It only remained to prove the position and stereochemistry of the carboxyl group. From the biogenetic point of view, the most probable positions for the location of the carboxyl group are 23 (or 24), 28 and 29 (or 30). However, recently triterpenes with oxygenated function at C-25[7] and C-27[8] have been found. It appears that it would be possible to find in nature a carboxyl group in any of the positions occupied by methyl groups in the oleanane skeleton.

As a preliminary approach, LAH reduction of ethyl jacquinate triacetate (IIg) gave the tetrol (IIIb). All attempts to form the isopropylidene derivative were unsuccessful and, therefore, this excludes C-23 (or C-24) for the newly formed hydroxyl group.

The transformation of jacquinic acid (IIa) to primula genin A (Ia), excludes C-28 for the location of the carboxyl group. While positions at C-25, C-26 and C-27 were considered unlikely due to the ease of saponification of the jacquinic esters, the carboxyl group is most probably located at C-29 (or C-30)—jacquinic acid being a C-29 (or C-30) carboxyl derivative of primula genin A. In order to correlate jacquinic acid (IIa) with queretaroic acid (VIa),[9,10] ethyl jacquinate diacetate (IIe)[11] was dehydrated by vigorous treatment with phosphorous oxychloride in pyridine. The anhydro compound so obtained (IVb) was catalytically hydrogenated to give V. This product was reduced with LAH to the triol (VIIa), whose triacetate was identical in all respects to queretarol triacetate obtained by LAH reduction of methyl queretaroate diacetate (VIb).[10] By these series of reactions the position and stereochemistry of the carboxyl group on jacquinic acid was shown to be 30β axial, as in IIa.[12] Jacquinic acid is, therefore, 3β,16α,28-trihydroxy-β amyrin-30β-oic acid. Another β-amyrin derivative, mirtillogenic acid[13] possesses the same distribution of its functional groups but differs in the stereochemistry at C-16 and C-20.

As model experiments for the last series of reactions described, the dehydration of primula genin A diacetate (Ib) and the subsequent catalytic hydrogenation to

[6] C. Djerassi, R. N. McDonald and J. J. Lemin, *J. Amer. Chem. Soc.* **75**, 5940 (1953).

[7] D. H. R. Barton, A. Hameed and J. F. McGhie, *J. Chem. Soc.* 5176 (1962).

[8] J. O. Knight and D. E. White, *Tetrahedron letters* No. 3, 100 (1961); A. R. H. Cole, D. T. Downing, J. C. Watkins and D. E. White, *Chem. & Ind.* 254 (1955).

[9] Queretaroic acid was kindly supplied by Dr. T. Ríos, of this Institute.

[10] C. Djerassi, J. A. Henry, A. J. Lemin and T. Ríos, *Chem. & Ind.* 1520 (1950); C. Djerassi, J. A. Henry, A. J. Lemin, T. Ríos and G. H. Thomas, *J. Amer. Chem. Soc.* **78**, 3783 (1956).

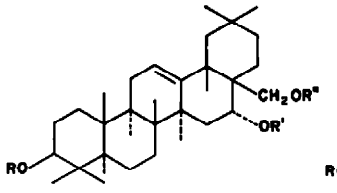
[11] It was assumed that on mild acetylation the axial 16α-hydroxyl group would remain free (Ref. 6), although it has been recently reported that mild acetylation of primula genin A (Ia) gave two diacetates Ib and Id, see R. V. Rao and P. K. Bose, *Tetrahedron* **18**, 461 (1962).

[12] C. Djerassi *et al.* showed unequivocally that the hydroxy-methylene group in queretaroic acid is 30β axial.

[13] C. Djerassi and G. H. Monsimer, *J. Amer. Chem. Soc.* **79**, 2901 (1957).

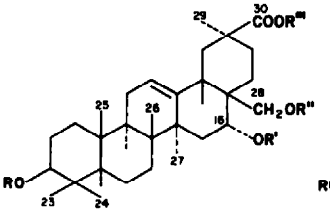
erythrodiol diacetate were carried out. In our hands both reactions needed more drastic conditions than used by previous workers[6,11,14].

Mild oxidation of ethyl jacquinate (IIc) with chromium trioxide in pyridine afforded two products. Structure IXa was assigned to the first product mainly on the basis of the spectroscopic data (experimental) and analytical data, which indicated the empirical formula $C_{31}H_{46}O_4$. The analytical data of the second compound showed that it had not lost any carbon atoms ($C_{32}H_{48}O_5$). The NMR spectrum did not show the characteristic signal of an aldehyde proton. Its IR spectrum showed the presence of hydroxyl group. On this basis, structure IXb was proposed for this compound.



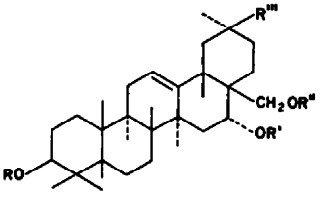
I

a; R = R′ = R″ = H
b; R = R″ = Ac; R′ = H
c; R = R′ = R″ = Ac
d; R = R′ = Ac; R″ = H



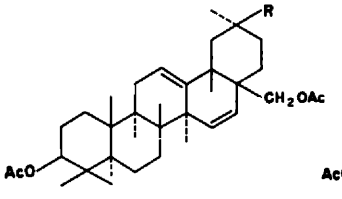
II

a; R = R′ = R″ = R‴ = H
b; R = R′ = R″ = H; R‴ = CH_3
c; R = R′ = R″ = H; R‴ = C_2H_5
d; R′ = H; R = R″ = Ac; R‴ = CH_3
e; R′ = H; R = R″ = Ac; R‴ = C_2H_5
f; R = R′ = R″ = Ac; R‴ = CH_3
g; R = R′ = R‴ = Ac; R‴ = C_2H_5



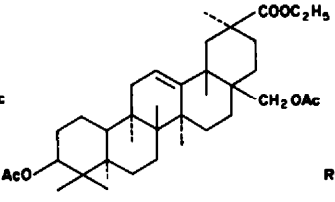
III

a; R = R′ = R″ = Ac; R‴ = CH = O
b; R = R′ = R″ = H; R‴ = CH_2OH
c; R = R″ = Ac; R′ = H; R‴ = CH_2OAc
d; R = R′ = R″ = Ac; R‴ = CH_2OAc

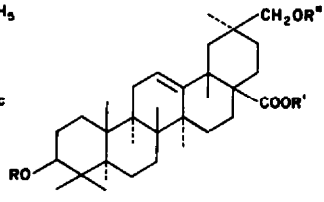


IV

a; R = CH_3
b; R = $COOC_2H_5$

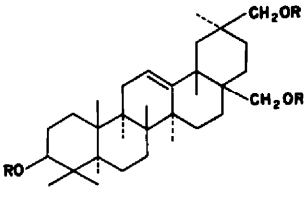


V



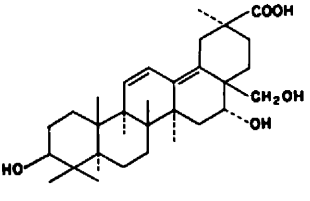
VI

a; R = R′ = R″ = H
b; R = R″ = Ac; R′ = CH_3

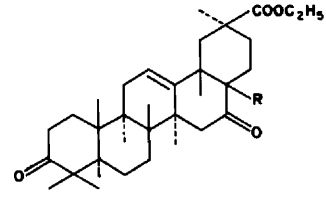


VII

a; R = H
b; R = Ac



VIII



IX

a; R = H
b; R = CH_2OH

[14] D. Frazier, C. R. Noller, *J. Amer. Chem. Soc.* **66**, 1267 (1944).

EXPERIMENTAL[15]

Isolation of the triterpenes from Jacquinia pungens

Green fruits. The ground and wet fruits of *Jacquinia pungens* (Theophrastaceae)[16] (4·6 k) was extracted with EtOH (20 l) by heating under reflux for 8 hr. The ethanolic extract was concentrated to 5 l and 50% HCl (500 ml) added. The solution was heated under reflux for 6 hr and diluted with water (20 l). The resinous precipitate was collected, washed with water and dried (wt. 119 g). The powdered precipitate was extracted by heating under reflux with hexane (2 l). The hexane extract was concentrated almost to dryness. The crystalline precipitate was collected, yielding 7 g, m.p. 243–245. Several crystallizations from acetone–hexane raised the m.p. to 248–249°; $[\alpha]_D$ +44·1°; ν_{max}; 3330 cm^{-1} (hydroxyl groups). It was identified as primula genin A by the standard methods. (Found: C, 78·31; H, 10·47. Calc. for $C_{30}H_{50}O_3$: C, 78·55; H, 10·99.)

The resin was then extracted with benzene (2 l), under reflux. The benzene solution was in turn extracted with a sat. $NaHCO_3$ aq. Chromatography of the neutral fraction on alumina yielded more primula genin A (4·5 g). The alkaline solution was acidified and the precipitate extracted with isopropyl ether. The solvent was evaporated to dryness and the solid residue dissolved in MeOH was esterified with diazomethane. The crude methyl ester was purified by chromatography on alumina. Elution with benzene–ethyl acetate (1:1) gave methyl jacquinate (IIb; 700 mg), m.p. 245–247°. Further crystallizations from acetone–hexane raised the m.p. to 249–250°; $[\alpha]_D$ +32·7°; ν_{max}; 3370 cm^{-1} (hydroxyl groups), 1717 cm^{-1} (ester group). (Found: C, 73·88; H, 10·04; O, 15·95. Calc. for $C_{31}H_{50}O_5$: C, 74·06; H, 10·03; O, 15·91%.)

Jacquinic acid (IIa). The methyl ester (IIb; 500 mg) was heated under reflux with 2% ethanolic KOH (30 ml) for 4 hr, diluted then with water and acidified. The precipitate was collected, washed with water and crystallized from methanol–acetone, yielding 390 mg, m.p. 310–312°; $[\alpha]_D$ +49·3°; ν_{max}; 3380 cm^{-1} (hydroxyl groups), 1690 cm^{-1} (carbonyl group). (Found: C, 73·47; H, 10·51; O, 16·27. Calc. for $C_{30}H_{48}O_5$: C, 73·73; H, 9·90; O, 16·37 %).

Mature fruits. The wet, ground fruits (750 g) were extracted and the glycosides hydrolysed as described above. The dry resin obtained (41 g) was extracted with hexane. The hexane solution was concentrated to a small volume yielding crystalline ethyl jacquinate (IIc; 510 mg), m.p. 208–210°. The mother liquors were chromatographed on alumina. Elution with benzene–ethyl acetate (1:1) gave more ethyl jacquinate (2·25 g) m.p. 215–217°. The analytical sample showed m.p. 220–221° (needles from acetone–hexane); $[\alpha]_D$ +74·8°; ν_{max}; 3400 cm^{-1} (hydroxyl group), 1710 cm^{-1} (ester group). (Found: C, 74·86; H, 10·09; O, 15·40. Calc. for $C_{32}H_{52}O_5$: C, 74·37; H, 10·14; O, 15·48%.)

The resin was then extracted by refluxing with isopropylether (1 l.). Concentration of the solution afforded jacquinic acid (IIa; 1·5 g) m.p. 307–308°.

Saponification of ethyl jacquinate (IIc). The ester (IIc; 2 g) was saponified in EtOH solution with KOH as in the case of the methyl ester (IIb). Crystallization from methanol–acetone yielded 2·51 g, m.p. 307–308°. It was identified with jacquinic acid by the standard methods.

Primula genin A diacetate (Ib). The diacetate (acetic anhydride and pyridine, 30 min on the steam bath) showed m.p. 187–188° (small needles) from acetone–hexane.[7]

Primula genin A triacetate (Ic). The triacetate (acetic anhydride and pyridine 2 hr on the steam bath) showed m.p. 152–153° (needles from aq. MeOH). (Found: C, 73·72; H, 9·39; O, 16·91. Calc. for $C_{36}H_{56}O_6$: C, 73·93; H, 9·65; O, 16·42%.)

Methyl jacquinate diacetate (IId). The diacetate (IIb) acetic anhydride and pyridine, 1 hr on the steam bath), showed m.p. 244–245° (needles from ether–hexane); ν_{max}; 3640 cm^{-1} (hydroxyl group), 1728 cm^{-1} (acetyl and ester groups). The NMR spectrum showed two singlets at 122 and 125 c/s. (intensity three protons each) corresponding to the acetyl groups. (Found: C, 71·60; H, 9·07; O, 19·24. Calc. for $C_{35}H_{54}O_7$: C, 71·64; H, 9·28; O, 19·09%.)

Methyl jacquinate triacetate (IIf). The triacetate (IIf) (acetic anhydride and pyridine, 4 hr on the steam bath), showed m.p. 176–178° (needles from ether–hexane); ν_{max}; 1715 cm^{-1} (acetyl and

[15] M.ps are uncorrected. IR spectra were run in $CHCl_3$ solution on a Perkin-Elmer double beam spectrophotometer. Rotations were determined in MeOH (unless noted otherwise). We are indebted to Syntex, S. A. for these determinations. The microanalyses were performed by Dr. Franz Pascher, Bonn, Germany.

[16] We are grateful to Mr. Arturo Gómez Pompa of the Instituto de Biología for the classification of the plant.

ester groups). A complex signal centered at 125 c/s (intensity 9 protons) is responsible for the three acetyl groups. (Found: C, 71·25; H. 8·79; O, 20·36. Calc. for $C_{37}H_{56}O_8$: C, 70·67; H, 8·98; O, 20·36%.)

Ethyl jacquinate diacetate (IIe). The diacetate (IIe; acetic anhydride and pyridine, 30 min on the steam bath), showed m.p. 188–190°; $[\alpha]_D$ +4·2°; ν_{max} 3490 (hydroxyl group); 1725 cm^{-1} (acetyl and ester groups). (Found: C, 72·30; H, 9·36; O, 18·35. Calc. for $C_{36}H_{56}O_7$: C, 71·96; H, 9·40; O, 18·64%.)

Ethyl jacquinate triacetate (IIg). The triacetate (IIg; acetic anhydride and a drop of perchloric acid at room temp. for 30 min) showed m.p. 167–169°; ν_{max}; 1730, 1740 cm^{-1} (acetyl and ester groups). (Found: C, 70·70; H, 9·06; O. 19·96. Calc. for $C_{36}H_{56}O_8$: C, 70·99; H, 9·09; O, 19·91).

Lithium aluminium hydride reduction of ethyl jacquinate (IIc). To a solution of the ester (IIc; 500 mg) in anh. tetrahydrofurane (100 ml) was added LAH (500 mg) and the mixture heated under reflux for 6 hr. The hydride was decomposed with ethyl acetate, water was then added. The solution was acidified with dil. HCl and extracted with ethyl acetate. The organic layer was washed with water, dried and evaporated to dryness. The residue was crystallized from acetone, yielding the tetrol (IIIb; 310 mg), m.p. 274–275°; $[\alpha]_D$ +33·7°; ν_{max} (Nujol); 3300 cm^{-1} (hydroxyl groups). (Found: C, 75·92; H, 10·58; O, 13·45. Calc. for $C_{30}H_{50}O_4$: C, 75·90; H, 10·62; O, 13·48%.)

Attempt to form the isopropylidene derivative, with acetone and acid catalysts under varying conditions, were unsuccessful.

Tetrol triacetate (IIIc). The triacetate (IIIc; acetic anhydride and pyridine, room temp. overnight) showed m.p. 217–218°, $[\alpha]_D$ +43·8°; ν_{max}; 3300 cm^{-1} (hydroxyl group), 1725 cm^{-1} (acetyl groups). (Found C, 72·54; H 9·19; O, 18·65. Calc for $C_{36}H_{56}O_7$: C 71·96, H, 9·40; O, 18·64%.)

Tetrol tetracetate (IIId). The tetracetate (IIId; acetic anhydride and a drop of perchloric acid, 30 min at room temp), showed m.p. 97–100° (needles from ether–hexane) $[\alpha]_D$ +17·8°; ν_{max}; 1740 cm^{-1} (acetyl groups). (Found: C, 71·15; H, 9·42; Calc. for $C_{38}H_{58}O_8$: C, 70·99; H, 9·09%.)

Rosenmund reduction of jacquinic acid (IIa). A solution of jacquinic acid (IIa; 500 mg) was treated with acetic anhydride (8 ml) and a drop of perchloric acid. After 1 hr at room temp, the mixture was poured into ice. The oily precipitate was extracted with ether. The organic layer was washed with water, dried and evaporated to dryness. The crude triacetate dissolved in benzene (10 ml) was treated with oxalyl chloride (5 ml) and heated under reflux for 3 hr. The volatile components were eliminated *in vacuo*. The crude acid chloride (ν_{max}; 1730 cm^{-1}) was dissolved in anhydrous toluene (40 ml), 10% Pd—$BaSO_4$ (300 mg) was added and with mechanical stirring, under reflux a strong stream of H_2 was passed through the solution. The HCl evolution was followed by titration. After 2 hr the evolution of HCl ceased. The catalyst was filtered off, the solvent evaporated to dryness *in vacuo* and the residue dissolved in ether. The ethereal solution was extracted with dil NaOH aq and washed with water. The solvent was evaporated to dryness and the residue was treated with Girard reagent. The carbonylic fraction was chromatographed on alumina. Elution with benzene–ether (10:1) gave the aldehyde (IIIa). Crystallization from aq. MeOH yielded small needles (300 mg) m.p. 103–108°; $[\alpha]_D \pm 0$; ν_{max}; 2720 cm^{-1} (aldehyde group), 1735 cm^{-1} (aldehyde and acetyl groups). The NMR showed a singlet at 572 c/s. (intensity 1 proton, corresponding to the hydrogen of the aldehyde group). (Found: C, 71·23; H, 9·32. Calc. for $C_{36}H_{54}O_7 \cdot \frac{1}{2} H_2O$: C, 71·20; H, 9·07%.)

Primula genin A (Ia), *by reduction of the aldehyde* (IIIa). The aldehyde (IIIa; 200 mg) in EtOH (6 ml) and diethyleneglycol (20 ml) was treated with hydrazine (2 ml), heated under reflux for 1 hr, KOH (150 mg) added and the mixture again heated under reflux for 1 hr. After 10 ml had been distilled off the solution was again refluxed for 3 hr and then diluted with water. The precipitate was extracted with ethyl acetate, washed with water and evaporated to dryness. The residue was dissolved in benzene and chromatographed on alumina. The crystalline fractions were recrystallized from acetone–hexane yielding needles (60 mg), m.p. 243–245°. This triol was identified with primula genin A by mixed m.p. determination and comparison of the IR spectra.

Erithrodiol from primula genin A (Ia). Primula genin A diacetate (Ib; 200 mg) in pyridine (5 ml) was treated with $POCl_3$ (0·5 ml) and heated under reflux for 16 hr. The solution was then poured onto ice and extracted with ethyl acetate. The organic layer was washed with 5% HCl aq and water. It was then dried and evaporated to dryness. The residue was crystallized from acetone–hexane yielding the anhydro derivative (IVa[11]; 70 mg), m.p. 215–217°; ν_{max} 1725 cm^{-1} (acetyl groups). (Found: C, 77·78; H, 10·00; O, 12·19. Calc. for $C_{34}H_{52}O_4$: C, 77·82; H, 9·99; O, 12·20%.)

The anhydro derivative (IVa; 50 mg) in acetic acid (10 ml) and a drop of perchloric acid was

hydrogenated with Adams catalyst (100 mg) for 24 hr. The catalyst was filtered off, the solution diluted with water and extracted with ethyl acetate. The organic layer was washed with water, $NaHCO_3$ aq, dried and evaporated to dryness. The residue was saponified and chromatographed on alumina. The crystalline fractions eluted with benzene–chloroform (4:1) were combined and crystallized from acetone–hexane yielding needles (30 mg) m.p. 215–218°. It was identified as erithrodiol by mixed m.p. and IR spectrum with an authentic sample.

Lithium aluminium hydride reduction of methyl queretaroate diacetate (VIb). The ester (VIb; 500 mg) in anh. tetrahydrofurane (100 ml) was treated with LAH (500 mg) and the mixture heated under reflux for 7 hr and worked up as in the previous case. The crude product was dissolved in benzene and chromatographed on alumina. Elution with benzene–ethyl acetate (4:1) afforded queretarol (VIIa; 350 mg), m.p. 280–281°; fluffy needles from acetone; $[\alpha]_D$ +71·9°; ν_{max} (KBr); 3350 cm^{-1} (hydroxyl group). (Found: C, 78·39; H, 10·97; O, 11·18. Calc. for $C_{30}H_{50}O_3$: C, 78·55; H, 10·99; O, 10·46%.)

Queretarol triacetate (VIIb). The triacetate (VIIb) (acetic anhydride and pyridine, on the steam bath for 4 hr) showed m.p. 135–137° (small needles from aq. MeOH); ν_{max}; 1730 cm^{-1} (acetyl groups). (Found: C, 73·52; H, 9·83; O, 16·89. Calc. for $C_{36}H_{56}O_6$: C, 73·83; H, 9·65; O, 16·42%.)

Dehydration of ethyl jacquinate diacetate (IIe). The diacetate (IIe; 400 mg) in pyridine (10 ml) was treated with $POCl_3$ (4 ml) heated under reflux for 16 hr and then worked up as above. The anhydro derivative (IVb), crystallized from hexane as needles (215 mg), m.p. 168–170°; $[\alpha]_D$ +74·5°; ν_{max}; 1725 cm^{-1} (acetyl groups). The NMR spectrum showed a complex signal centered at 325 c/s corresponding to 3 vinylic protons. (Found: C, 74·16; H, 9·32; O, 16·75. Calc. for $C_{36}H_{54}O_6$: C, 74·19; H, 9·34; O, 16·47%.)

Hydrogenation of the anhydro compound (IVb). The anhydro derivative (IVb; 200 mg) in acetic acid (50 ml) and a drop of perchloric acid was hydrogenated on PtO_2 (500 mg). Crystallization from hexane yielded the dihydroderivative (V; 160 mg); m.p. 180–188°. Several crystallization from hexane raised the m.p. to 188–190°; $[\alpha]_D$ +90·12; ν_{max}; 1725 cm^{-1} (acetyl and ester groups). A singlet at 316 c/s in the NMR spectrum indicates 1 vinylic proton. (Found: C, 74·49; H, 9·47; O, 16·26. Calc. for $C_{36}H_{56}O_6$: C, 73·93; H, 9·65; O, 16·42%.)

Lithium aluminium hydride reduction of the dihydroderivative (V). Compound V (140 mg) in tetrahydrofurane (100 ml) was reduced with LAH (350 mg), under reflux for 4 hr. Chromatography on alumina and crystallization from acetone gave 90 mg; m.p. 281–283°; [α] +72·1°; mixed m.p. with queretarol (VIIa) showed no depression.

The triacetate (VIIb; m.p. 133–136°, showed no depression in mixed m.p. determination with authentic queretarol triacetate (VIIIb) and the IR spectra were identical.

Selenium dioxide oxidation of ethyl jacquinate triacetate (IIg). To a solution of the triacetate (IIg; 200 mg) in acetic acid (15 ml) was added SeO_2 (400 mg) and the mixture heated under reflux for 20 hr. The oily product obtained was saponified with 2% methanolic KOH. The acid (VIII; 150 mg) was crystallized from acetone, m.p. 270–272°; ν_{max} (KBr) 3450 cm^{-1} (hydroxyl groups), 1700 cm^{-1} carboxyl group), 1635 cm^{-1} (double bonds); λ_{max} 244, 252 and 261 mμ; log. ε, 4·39, 4·47, 4·27. (Found: C, 74·26; H, 9·31; O, 16·75. Calc. for $C_{30}H_{46}O_6$: C, 74·03; H, 9·53; O, 16·45%.)

Chromium trioxide oxidation of ethyl jacquinate (IIc). The ester (IIc; 500 mg) in pyridine (10 ml) was treated with a solution of CrO_3 (500 mg) in pyridine (20 ml) at room temp for 20 hr. The oily product obtained was chromatographed on alumina. Elution with benzene gave the diketone (IXa), the analytical sample showed m.p. 170–172° (needles from ether–hexane); ν_{max}; 1710 cm^{-1} (six membered ketones and ester group). (Found: C, 77·10; H, 9·57; O, 13·74. Calc. for $C_{31}H_{46}O_4$: C, 77·13; H, 9·61; O, 13·26%.)

Elution with benzene–ether (10:1) afforded the hydroxydiketone (IXb), m.p. 156·5–157·5° needles from ether–hexane); ν_{max}; 3700 cm^{-1} (hydroxyl groups), 1730 cm^{-1} (ester group), 1710 cm^{-1} (six membered ketones). The NMR spectrum did not show the signal corresponding to the proton of an aldehyde group. (Found: C, 74·86; H, 9·39; O, 16·07. Calc. for $C_{32}H_{48}O_5$; C, 74·96; H, 9·44; O, 15·60%.)