Bitter Principles of Aquifoliaceae. III.[1] The Structures and Stereochemistry of Three Aglycones Obtained by the Hydrolysis of Latifoloside A, a Bitter Glycoside from *Ilex latifolia* Thunb.

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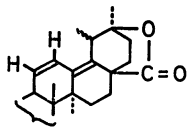
From the leaves of *Ilex latifolia* Thunb., two new bitter glycosides, latifoloside, A and B, have been isolated. The acid hydrolysis of A afforded three triterpenoid aglycones, which have been formulated by spectroscopic and chemical evidence as I, II, and III respectively.

In the course of an investigation of the bitter principles of Aquifoliaceae plants, the constituents of the leaves of *Ilex latifolia* Thunb., which have an intense bitter taste, have been examined. A methanol extract of fresh leaves was treated with *n*-butanol, the subsequent chromatography of the soluble material over silicic acid led to the isolation of two bitter glycosides, latifoloside A (0.009% yield) (mp 235—236 °C (decomp.), $[\alpha]_D^{24}$ −33° (*c* 1.0, ethanol)) and B (0.001% yield) (mp 210—211 °C (decomp.), $[\alpha]_D^{16}$ −11° (*c* 0.1, pyridine)). Latifoloside A, which has been obtained in a major amount, yielded three triterpenoid aglycones, I, II, and III, on hydrolysis with methanol–1M sulfuric acid. In this paper, we will deal with the structural elucidation of these three compounds.

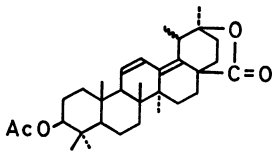
Results and Discussion

Aglycone I, $C_{31}H_{46}O_4$ (mp 269—270 °C, $[\alpha]_D^{25}$ −110° (*c* 1.0, ethanol)), shows a hydroxylic absorption in the IR spectrum at 3400 cm^{-1} and forms a monoacetate IV, $C_{33}H_{48}O_5$ (mp 272—273 °C), the IR spectrum of which no longer exhibits a hydroxyl group. The NMR spectrum of IV shows signals due to an acetyl group at δ 2.04 and a methoxyl group at δ 3.12. In addition, the signal of the methine proton on the oxygenated carbon of I at δ 3.22 shifts to 4.49 on acetylation. These observations indicate that the hydroxyl group of I is secondary, and the methoxyl group, tertiary.

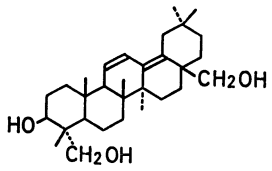
On the other hand, I exhibits UV maxima at 253 (shoulder), 261, and 270 (shoulder) nm (ε 24500, 30000, and 21500 respectively), an IR band at 1750 cm^{-1}, and NMR signals at δ 1.41 (3H, s), 5.74 (1H, dd, J=11 and 2 Hz), and 6.77 (1H, dd, J=11 and 3 Hz). The similarity of these spectral data to those of the dienelactone V[2] suggests the presence of the partial structure Ia. Further evidence in support of this partial structure was provided by the following chemical transformations. The reduction of I with lithium aluminum hydride, followed by acetylation, gave a monoacetate VI, $C_{33}H_{50}O_4$ (mp 210—211 °C), the UV absorptions of which are quite similar to those of VII.[3] The treatment of the epoxide VIII[4] in the same way as in the formation of V[2] afforded a lactone IX, $C_{34}H_{48}O_6$ (mp 241—242 °C), which exhibits UV maxima at 252, 260, and 269 nm (ε 19300, 23800, and 16600 respectively), an IR band at 1750 cm^{-1}, and NMR signals at δ 1.40 (3H, s), 5.68 (1H, dd, J=11 and 2 Hz), and 6.10 (1H, dd, J=11 and 3 Hz), all supporting the partial structure Ia for aglycone I.



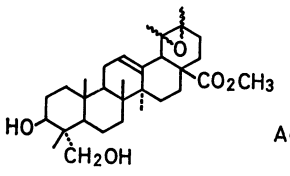
Ia



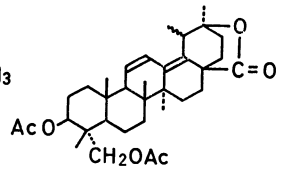
V



VII



VIII



IX

These facts and the analogy with the structures of the congeners isolated from *Ilex latifolia* Thunb.[5] lead to the assignment of the ursane skeleton for I, in which the partial structure Ia would constitute the C, D, and E-rings.

The location and the configuration of the tertiary methoxyl group were proved as follows. In the NMR spectrum of IX, the signal due to the C-19 methyl protons appears as a doublet at δ 1.08 as a result of the coupling with the allylic methine proton, which appears as a quartet at δ 2.66. On the other hand, the NMR spectrum of I does not show the corresponding signals, but a singlet at δ 1.45 assigned to the methyl protons on an oxygenated carbon. Hence, the methoxyl group in question must be located at C-19. In the

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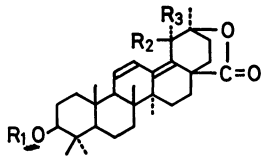
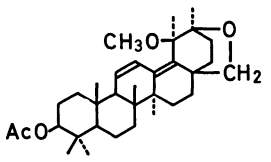
NMR spectrum of VI, the signal of the C-19 methyl protons shifts to a higher field (δ 1.36) compared with that of IV, while the signal of the methoxyl group appears at a lower field (δ 3.26) than that of IV. Taking account of the anisotropy of the lactonic carbonyl group, these observations indicate that the C-19 methyl group lies near the plane of the carbonyl group (α-oriented) and the methoxyl group above the plane (β-oriented).

On biogenetic grounds, it is most reasonable to place the secondary hydroxyl group in I at the C-3 position. Moreover, the NMR spectrum of IV shows a signal due to the methine proton attached to the carbon atom bearing an acetoxyl group at δ 4.49 (1H, t-like, W1/2 18 Hz), the shape and position of which correspond to those found in the spectra of C-3 equatorial acetates in the polyterpenes.[6]

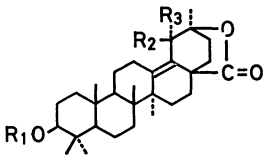
Finally, the structure was confirmed by correlation with vanguerolic acid lactone, X.[2] The hydrogenolysis of I in glacial acetic acid over a platinum catalyst did give X, $C_{30}H_{46}O_3$ (mp and mixed mp 263—267 °C), along with a dihydro-compound which forms a monoacetate XI, $C_{33}H_{50}O_5$ (mp 247—249 °C). Therefore, the I structure must represent aglycone I.

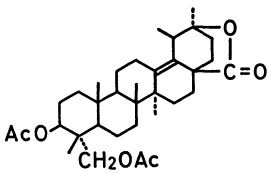




VI

I R_1=H, R_2=OCH_3, R_3=CH_3
II R_1=H, R_2=OH, R_3=CH_3
III R_1=H, R_2=CH_3, R_3=OH
IV R_1=Ac, R_2=OCH_3, R_3=CH_3
XV R_1=Ac, R_2=OH, R_3=CH_3
XVI R_1=Ac, R_2=CH_3, R_3=OH



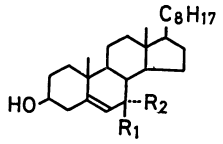


XIX

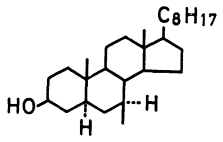
X R_1=H, R_2=CH_3, R_3=H
XI R_1=Ac, R_2=OCH_3, R_3=CH_3
XVII R_1=H, R_2=OH, R_3=CH_3
XVIII R_1=H, R_2=CH_3, R_3=OH

Furthermore, the conversion of I into X determines the configurations at C-19 of not only X, but also V** and IX, which have hitherto remained unknown. Callow and Thompson have reported that the hydrogenolysis of XII over a platinum catalyst gave XIII in glacial acetic acid and XIV in ethyl acetate, with an inversion at C-7 by means of the S_N2 mechanism.[7]

** The hydrogenation of V affords X under the same conditions.[2]



XII R_1=OH, R_2=CH_3
XIV R_1=CH_3, R_2=H



XIII

These facts suggest that C-19 methyl groups of X, V, and IX are β-oriented.

Aglycone II, $C_{30}H_{44}O_4$ (mp 227—229 °C, $[\alpha]_D^{18}$ −90° (c 0.15, ethanol)), exhibits UV maxima at 251 (shoulder), 259, and 268 (shoulder) nm (ε 21000, 26900, and 19100 respectively), IR bands at 3500 and 1730 cm^{-1}, and NMR signals at δ 1.42 and 1.51 (3H each, s), 3.20 (1H, t-like, W1/2 18 Hz), 5.74 (1H, dd, J=11 and 2 Hz), and 6.83 (1H, dd, J=11 and 3 Hz), suggesting the presence of the same partial structure as in I. II forms a monoacetate XV, $C_{32}H_{46}O_5$ (mp 259—261 °C), the IR spectrum of which still shows a hydroxylic absorption at 3420 cm^{-1}. These observations indicate the presence of a hydroxyl group at C-19 in II instead of the methoxyl group in I.

A close structural similarity of aglycone III, $C_{30}H_{44}O_4$ (mp 265—267 °C, $[\alpha]_D^{18}$ −147° (c 0.1, ethanol)), to II is indicated by the spectral data, showing UV maxima at 253 (shoulder), 261, and 270 (shoulder) nm (ε 16500, 20100, and 14200 respectively), IR bands at 3440 and 1720 cm^{-1}, and NMR signals at δ 1.38 and 1.45 (3H each, s), 3.21 (1H, t-like, W1/2 18 Hz), 5.78 (1H, dd, J=11 and 2 Hz), and 6.88 (1H, dd, J=11 and 3 Hz). III forms a monoacetate XVI, $C_{32}H_{46}O_5$ (mp 268—270 °C), the IR spectrum of which still shows a hydroxylic absorption at 3400 cm^{-1}. From these data, it may be concluded that II and III are epimers with respect to C-19.

In order to determine the configuration at C-19, the hydrogenolysis of II and III was attempted in a way similar to that used with I. Thus, II afforded X along with a dihydro-compound XVII, $C_{30}H_{46}O_4$ (mp 247—249 °C), whereas III yielded only a dihydro-compound XVIII, $C_{30}H_{46}O_4$ (mp 259—261 °C). In addition, the UV absorptions of II characteristic of the partial structure Ia disappeared after 4 hr, while those of III disappeared within 1 hr. In the hydrogenolysis reaction of I, which gave X and a dihydro-compound, as has been mentioned above, the disappearance of UV absorptions was observed after 3 hr, while IX gave a dihydro-compound XIX after 1 hr. If we assume that the hydrogenolysis of the allylic C–O bond occurs with inversion by means of the S_N2 mechanism and that the hydrogenation rate is affected only by the ease in approach to the catalyst, these results suggest that the configuration at C-19 of II is similar to that of I, while III and IX have the same configuration at C-19. The catalyst would attack the α-face of the molecule because of the steric hindrance due to the methyl groups at C-8 and C-10. The α-oriented methyl group at C-19 prevents the approach to the catalyst, whereas the α-oriented hydroxyl group promotes the reaction through its affinity for the catalyst metal.

Experimental

The NMR spectra were determined on a JEOL PS-100 (100 MHz) spectrometer in deuterochloroform solutions, with tetramethylsilane as the internal standard. The IR spectra were recorded on a JASCO model IR-S spectrophotometer. The UV data were measured in ethanol solutions with a Hitachi EPS-3T spectrophotometer. A Rex Optical Works apparatus, model NEP-2, was used for the measurement of the rotations. Column chromatography was performed using Mallinckrodt silicic acid. The mps were determined in glass capillaries and are uncorrected.

Isolation. The fresh leaves of *Ilex latifolia* Thunb. (26 kg), collected in Kochi City in July, 1973, were chopped up and extracted with hot methanol (120 l). After treatment with activated carbon, the extract was concentrated up to about 6 l, leaving an aqueous solution. This solution, after filtration, was extracted with ethyl acetate (1.5 l×3) and then with *n*-butanol (1.5 l×3). The *n*-butanol layer, which has an intense bitter taste, was evaporated *in vacuo* to afford a dark brown residue, which was dissolved in methanol (600 ml). The methanol solution was poured into ether (9 l), and the resulting precipitates were collected by filtration, washed with ether, and dried to give a yellowish-white powder (432 g). This powder was repeatedly chromatographed over silicic acid, with chloroform–methanol–water (80:20:2) as the eluent, to give latifoloside A and B.

Latifoloside A. The combined fractions (3.663 g) were recrystallized from acetone–methanol (2:1) at 50—55 °C to give pure latifoloside A as needles (2.256 g); mp 235—236 °C (decomp.), $[\alpha]_D^{24}$ −33° (*c* 1.0, EtOH), Molisch test (+), IR (KBr) 3400, 1720, and 1045 cm^{-1}.

Latifoloside B. The more polar fractions (1.107 g) were recrystallized from methanol to yield pure latifoloside B as needles (255 mg); mp 210—211 °C (decomp.), $[\alpha]_D^{16}$ −11° (*c* 0.1, pyridine), Molisch test (+), IR (KBr) 3400, 1695, and 1075 cm^{-1}.

Hydrolysis of Latifoloside A. To a solution of latifoloside A (2.0 g) in methanol (200 ml), we added 1 M sulfuric acid (200 ml). The mixture was refluxed for 5 hr and then extracted with ether (600 ml). The extract was washed with a sodium bicabonate solution and with water, dried over magnesium sulfate, and evaporated to dryness. The residue (948 mg) was chromatographed over silicic acid; subsequent elution with chloroform gave aglycone I, II, and III, in that order.

Aglycone I. The earliest fractions (284 mg) were recrystallized from methanol to give I as needles (180 mg); mp 269—270 °C, $[\alpha]_D^{32}$ −110° (*c* 1.0, EtOH), UV (EtOH) 253 (shoulder), 261, and 270 (shoulder) nm (ε 24500, 30000, and 21500 respectively), IR (KBr) 3400 and 1750 cm^{-1}, NMR ($CDCl_3$) δ 1.41 and 1.45 (3H each, s, C_{20} and C_{19}–CH_3), 3.12 (3H, s, O–CH_3), 3.22 (1H, t-like, C_3–H), 5.74 (1H, dd, J=11 and 2 Hz, C_{12}–H), and 6.77 (1H, dd, J=11 and 3 Hz, C_{11}–H), (Found: C, 75.45; H, 9.67%. Calcd for $C_{31}H_{46}O_4 \cdot 1/2H_2O$: C, 75.72; H, 9.63%).

Aglycone II. The middle fractions (254 mg) were recrystallized from aqueous methanol to yield II as prisms (168 mg); mp 227—229 °C, $[\alpha]_D^{18}$ −90° (*c* 0.15, EtOH), UV (EtOH) 251 (shoulder), 259, and 268 (shoulder) nm (ε 21000, 26900, and 19100 respectively), IR (Nujol) 3500, 1730, and 1050 cm^{-1}, NMR ($CDCl_3$) δ 1.42 and 1.51 (3H each, s, C_{20} and C_{19}–CH_3), 3.20 (1H, t-like, W1/2 18 Hz, C_3–H), 5.74 (1H, dd, J=11 and 2 Hz, C_{12}–H), and 6.83 (1H, dd, J=11 and 3 Hz, C_{11}–H), (Found: C, 77.34; H, 9.63%. Calcd for $C_{30}H_{44}O_4$: C, 76.88; H, 9.46%).

Aglycone III. The last fractions (300 mg) were recrystallized from aqueous methanol to give III as plates (204 mg); mp 265—267 °C, $[\alpha]_D^{16}$ −147° (*c* 0.1, EtOH), UV (EtOH) 253 (shoulder), 261, and 270 (shoulder) nm (ε 16500, 20100, and 14200 respectively), IR (KBr) 3440, 1720, and 1080 cm^{-1}, NMR ($CDCl_3$) δ 1.38 and 1.45 (3H each, s, C_{20} and C_{19}–CH_3), 3.21 (1H, t-like, W1/2 18 Hz, C_3–H), 5.78 (1H, dd, J=11 and 2 Hz, C_{12}–H), and 6.88 (1H, dd, J=11 and 3 Hz, C_{11}–H), (Found: C, 76.45; H, 9.56%. Calcd for $C_{30}H_{44}O_4$: C, 76.88; H, 9.46%).

Acetylation of I. A solution of I (40 mg) in acetic anhydride (2 ml) and pyridine (1 ml) was allowed to stand at room temperature overnight and then worked up in the usual way to give a white precipitate which was subsequently recrystallized from methanol to yield a monoacetate IV as needles (29 mg); mp 272—273 °C, IR (CCl_4) 1750, 1730, and 1245 cm^{-1}, NMR ($CDCl_3$) δ 1.41 and 1.45 (3H each, s, C_{20} and C_{19}–CH_3), 2.04 (3H, s, O–CO–CH_3), 3.12 (3H, s, O–CH_3), 4.49 (1H, t-like, W1/2 18 Hz, C_3–H), 5.71 (1H, dd, J=11 and 2 Hz, C_{12}–H), and 6.77 (1H, dd, J=11 and 3 Hz, C_{11}–H), (Found: C, 75.38; H, 9.33%. Calcd for $C_{33}H_{48}O_5$: C, 75.53; H, 9.22%).

Acetylation of II. II (37 mg) was treated with acetic anhydride (1 ml) and pyridine (1 ml) as has been described above, and the resulting precipitates were recrystallized from methanol to give a monoacetate XV as needles (30 mg); mp 259—261 °C, IR (Nujol) 3420, 1740, and 1255 cm^{-1}, NMR ($CDCl_3$) δ 1.41 and 1.51 (3H each, s, C_{20} and C_{19}–CH_3), 2.03 (3H, s, O–CO–CH_3), 4.51 (1H, t-like, W1/2 18 Hz, C_3–H), 5.76 (1H, dd, J=11 and 2 Hz, C_{12}–H), and 6.84 (1H, dd, J=11 and 3 Hz, C_{11}–H), (Found: C, 75.20; H, 9.15%. Calcd for $C_{32}H_{46}O_5$: C, 75.26; H, 9.08%).

Acetylation of III. III (50 mg) was treated with acetic anhydride (2 ml) and pyridine (2 ml) as has been described above, and the resulting precipitates were recrystallized from methanol to yield a monoacetate XVI as needles (35 mg); mp 268—270 °C, IR (Nujol) 3400, 1735, 1715, and 1235 cm^{-1}, NMR ($CDCl_3$) δ 1.38 and 1.45 (3H each, s, C_{20} and C_{19}–CH_3), 2.05 (3H, s, O–CO–CH_3), 4.51 (1H, t-like, W1/2 18 Hz, C_3–H), 5.78 (1H, dd, J=11 and 2 Hz, C_{12}–H), and 6.92 (1H, dd, J=11 and 3 Hz, C_{11}–H), (Found: C, 75.33; H, 9.17%. Calcd for $C_{32}H_{46}O_5$: C, 75.26; H, 9.08%).

Reduction of I with Lithium Aluminum Hydride. To a solution of I (50 mg) in tetrahydrofuran (5 ml), we added lithium aluminum hydride (10 mg) in tetrahydrofuran (5 ml). The mixture was stirred at room temperature for 1 hr and then poured into ether floated on water. The organic layer was washed with dilute hydrochloric acid and then with water. The subsequent drying and evaporation of the solution left a residue (48 mg) which no longer showed the lactonic band in the IR spectrum. The acetylation and recrystallization of the product from aqueous methanol afforded a monoacetate VI as needles (19 mg); mp 210—211 °C, UV (EtOH) 244, 253, and 262 nm (ε 18000, 25600, and 16000 respectively), IR (CCl_4) 1735 and 1245 cm^{-1}, NMR ($CDCl_3$) δ 1.16 (3H, s, C_{20}–CH_3), 1.34 (3H, s, C_{19}–CH_3), 2.04 (3H, s, O–CO–CH_3), 3.26 (3H, s, O–CH_3), 3.40 (2H, s, O–CH_2–), 4.51 (1H, t-like, C_3–H), 5.62 (1H, dd, J=11 and 2 Hz, C_{12}–H), and 6.85 (1H, dd, J=11 and 3 Hz, C_{11}–H), (Found: C, 75.60; H, 9.79%. Calcd for $C_{33}H_{50}O_4 \cdot 2/3H_2O$: C, 75.82; H, 9.77%).

Formation of the Lactone IX. The procedure of Barton *et al.*[2] was followed: the epoxide VIII (220 mg) in glacial acetic acid (18 ml) containing concentrated hydrochloric acid (2 ml) was heated at 100 °C for 10 min. The mixture was then worked up in the usual manner, and the resulting precipitates (236 mg) were recrystallized from aqueous methanol

to give a lactone IX as flakes (104 mg); mp 241—242 °C, UV (EtOH) 252, 260, and 269 nm (ε 19300, 23800, and 16600 respectively), IR (CCl_4) 1750 and 1245 cm^{-1}, NMR ($CDCl_3$) δ 1.08 (3H, d, J=7 Hz, C_{19}-CH_3), 1.40 (3H, s, C_{20}-CH_3), 2.02 and 2.06 (3H each, s, O-CO-CH_3), 2.66 (1H, q, J=7 Hz, C_{19}-H), 3.77 (2H, s, O-CH_2-), 4.77 (1H, m, C_3-H), 5.68 (1H, dd, J=11 and 2 Hz, C_{12}-H), and 6.10 (1H, dd, J=11 and 3 Hz, C_{11}-H), (Found: C, 73.92; H, 8.86%. Calcd for $C_{34}H_{48}O_6$: C, 73.88; H, 8.75%).

Hydrogenolysis of I. I (80 mg) and hydrated platinum oxide (40 mg) were stirred in glacial acetic acid (16 ml) under a hydrogen atmosphere at room temperature and normal pressure; after 3 hr, the UV absorptions at 250—270 nm almost disappeared. The catalyst was removed by filtration, and then the filtrate was evaporated. The residue was dissolved in ether, washed with a sodium bicarbonate solution and water, dried over magnesium sulfate, and evaporated to dryness. The residue was chromatographed over silicic acid; subsequent elution with chloroform gave a demethoxy-compound and a dihydro-compound.

The crude demethoxy-compound (32 mg) was recrystallized from aqueous methanol to yield vanguerolic acid lactone X as plates (25 mg); mp and mixed mp with an authentic sample,*** 263—267 °C, $[\alpha]_D^{16}$ −70° (c 0.1, EtOH).

The crude dihydro-compound (43 mg) was acetylated as has been described above, and the product was recrystallized from methanol to give a monoacetate XI as plates (21 mg); mp 247—249 °C, UV (EtOH) 231 nm (ε 5000), NMR ($CDCl_3$) δ 1.39 (6H, s, C_{19} and C_{20}-CH_3), 2.03 (3H, s, O-CO-CH_3), 3.27 (3H, s, O-CH_3), and 4.48 (1H, t-like, W1/2 18 Hz, C_3-H), (Found: C, 75.88; H, 9.72%. Calcd for $C_{33}H_{50}O_5$: C, 75.24; H, 9.57%).

Hydrogenolysis of II. II (78 mg) and hydrated platinum oxide (39 mg) in glacial acetic acid (16 ml) were treated as has been described above; after 4 hr, the UV absorptions at 250—270 nm almost disappeared. The residue was chromatographed over silicic acid; subsequent elution with chloroform–methanol (99: 1) yielded a deoxy-compound and a dihydro-compound.

The crude deoxy-compound (12 mg) was recrystallized from aqueous methanol to give X as plates (8 mg); mp and mixed mp with an authentic sample, 263—267 °C.

The crude dihydro-compound (48 mg) was recrystallized from aqueous methanol to yield XVII as plates (31 mg); mp 247—249 °C, UV (EtOH) 231 nm (ε 8600), IR (nujol) 3560 and 1735 cm^{-1}, (Found: C, 76.61; H, 9.89%. Calcd for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85%).

*** This sample was obtained by the method described in the literature[2] from methyl vanguerolate acetate, which has kindly been provided by Prof. D. H. R. Barton.

The acetylation of XVII (22 mg) and recrystallization of the product from chloroform–methanol afforded a monoacetate as needles (13 mg); mp 325—330 °C, IR (Nujol) 3510 and 1740 cm^{-1}, (Found: C, 75.16; H, 9.05%. Calcd for $C_{32}H_{48}O_5$: C, 74.96; H, 9.44%).

Hydrogenation of III. III (51 mg) in glacial acetic acid (10 ml) was hydrogenated in the presence of hydrated platinum oxide (26 mg) as has been described above; after 1 hr, the UV absorptions at 250—270 nm completely disappeared. The residue was recrystallized from methanol to give XVIII as prisms (39 mg); mp 259—261 °C, UV (EtOH) 229 nm (ε 5100), IR (Nujol) 3440 and 1715 cm^{-1}, (Found: C, 73.03; H, 10.18%. Calcd for $C_{30}H_{46}O_4 \cdot 5/4H_2O$: C, 73.06; H, 9.91%).

The acetylation of XVIII (33 mg) and recrystallization of the product from chloroform–methanol gave a monoacetate as needles (25 mg); mp 320—325 °C, IR (Nujol) 3470, 1740, and 1715 cm^{-1}, (Found: C, 75.02; H, 8.98%. Calcd for $C_{32}H_{48}O_5$: C, 74.96; H, 9.44%).

Hydrogenation of IX. IX (70 mg) and hydrated platinum oxide (35 mg) in glacial acetic acid (14 ml) were treated as has been described above; after 1 hr, the UV absorptions at 250—270 nm almost disappeared. The residue was recrystallized from aqueous methanol to yield XIX as needles (36 mg); mp 226—228 °C, UV (EtOH) 227 nm (ε 5100) IR (Nujol) 1740 cm^{-1}, NMR ($CDCl_3$) δ 1.10 (3H, d, J=7 Hz, C_{19}-CH_3), 1.37 (3H, s, C_{20}-CH_3), 2.01 and 2.05 (3H each, s, O-CO-CH_3), 2.55 (1H, qd, J=7 and 2 Hz, C_{19}-H), 3.70 and 3.86 (1H each, AB q, J_{AB}=12 Hz, O-CH_2-), and 4.77 (1H, t-like, W1/2 18 Hz, C_3-H), (Found: C, 73.60; H, 9.19%. Calcd for $C_{34}H_{50}O_6$: C, 73.61; H, 9.09%).

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