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247. *Sapogenins. Part VI. Quillaic Acid.*

By Donald F. Elliott and George A. R. Kon.

The sapogenin of quillaia bark is shown to have the formula $C_{30}H_{46}O_5$, not $C_{29}H_{44}O_5$ as previously supposed, and to be unsaturated. The acid is converted into a *diacetyl-lactone*, showing that the double bond occupies a $\beta\gamma$- or $\gamma\delta$-position with respect to the carboxyl group. Degradation experiments show that quillaic acid is an aldehyde and contains the group CH(OH)·C·CHO, doubtless situated in ring A. The position of the second hydroxyl group has not yet been determined, but it is shown that it cannot be in rings A or C. Quillaic acid is probably a hydroxygypsogenin.

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Quillaic acid is one of the most readily accessible triterpenes because quillaia saponin is largely used in commerce. The only definite data regarding its chemistry are due to Windaus, Hampe, and Rabe (*Z. physiol. Chem.*, 1926, **160**, 301), who described it as a saturated dihydroxyketo-acid, $C_{29}H_{44}O_5$, and prepared an ester, an oxime, and a diacetyl derivative. Ruzicka and van Veen (*ibid.*, 1928, **184**, 69) dehydrogenated quillaic acid on a small scale and obtained sapotalene (1 : 2 : 7-trimethylnaphthalene).

The principal difficulty encountered at the outset of our investigation was in the preparation of the pure sapogenin. The autoclave method of hydrolysis recommended by Windaus, Hampe, and Rabe (*loc. cit.*) is difficult to carry out and we have found that equally good results can be achieved by somewhat prolonged hydrolysis of the saponin with dilute acid. It is essential to free the crude sapogenin from sugars and humic substances, as in the analogous preparation of bassic acid (this vol., p. 1126). The yield of pure sapogenin is very poor, but a good deal of usable material can be recovered from the mother-liquors in the form of the diacetyl-lactone (see below).

The properties of the pure sapogenin correspond with those recorded by Windaus, Hampe, and Rabe (*loc. cit.*), but the pure preparation crystallised from ethyl acetate gives analysis figures in perfect agreement with the formula $C_{30}H_{46}O_5$ and this is confirmed by titrations of the acid and the analysis of numerous derivatives; specimens of the acid crystallised from other solvents are, however, apt to give low values on combustion comparable with those recorded by Windaus, Hampe, and Rabe (*loc. cit.*).

Contrary to earlier findings quillaic acid is unsaturated and gives a distinct colour with tetranitromethane. The acid is hydrogenated in presence of Adams's catalyst to *dihydroquillaic acid* (*methyl* ester, m. p. 269—270°), but this is formed by the reduction of the carbonyl group and the methyl ester accordingly has three active hydrogen atoms. The newly formed hydroxyl group occupies a position 1 : 3 with respect to another hydroxyl, because the methyl ester forms an *acetonyl* derivative, although slowly and in poor yield.

Dihydroquillaic acid is still unsaturated to tetranitromethane and the presence of a double bond situated in the $\beta\gamma$- or $\gamma\delta$-position with respect to the carboxyl group is shown by the formation of a saturated *triacetyl-lactone* with hydrogen bromide in acetic acid. The double bond is evidently an inert one, as in other sapogenins.

Like its dihydro-derivative, quillaic acid is readily lactonised to the *diacetyl-lactone*; from the very easy deacetylation of this to *quillaic lactone* it can be inferred that both hydroxyl groups of quillaic acid are primary or secondary.

The carboxyl group occupies a " protected " position, as in other sapogenins, although quillaic ester is hydrolysed rather more easily than the esters of other sapogenins.

The carbonyl group of quillaic acid offers the next point of attack. To avoid complications due to the double bond, the oxidation of the saturated diacetyl-lactone was first examined. The action of chromic acid leads to an *acid* with the same number of carbon atoms, $C_{34}H_{50}O_8$, readily deacetylated to the parent acid, $C_{30}H_{46}O_6$, which was characterised by its crystalline *methyl* ester. The formation of these products shows that quillaic acid is an aldehyde, and is exactly analogous to the oxidation of the bromo-lactone of acetylgypsogenin (Ruzicka, Giacomello, and Grob, *Helv. Chim. Acta*, 1938, **21**, 83). The C_{30} acid was further oxidised by chromic acid to a neutral compound, $C_{29}H_{42}O_4$; several acids were also produced which are still under investigation. The neutral compound forms a *mono-semicarbazone* and a *mono*-2 : 4-*dinitrophenylhydrazone*, but it is a diketone and no longer

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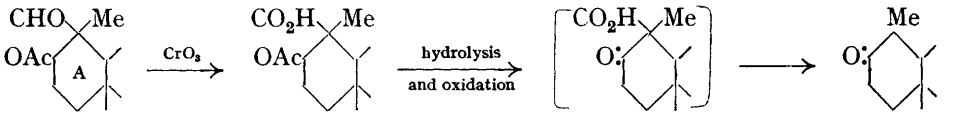
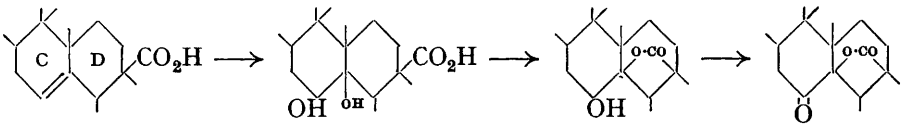
has an active hydrogen atom (Zerevitinov). The formation of this diketone is entirely analogous to the production of nor-β-boswellenone on oxidation of boswellic acid (Simpson and Williams, J., 1938, 686) and also of hedragone from gypsogenin (Ruzicka and Giacomello, *Helv. Chim. Acta*, 1937, **20**, 299) and involves the oxidation of a β-hydroxy-acid to the corresponding ketonic acid, which then loses carbon dioxide. Since quillaic acid is dehydrogenated to sapotalene, it may be assumed that it has the usual triterpene skeleton and the oxidation process may be formulated as follows :



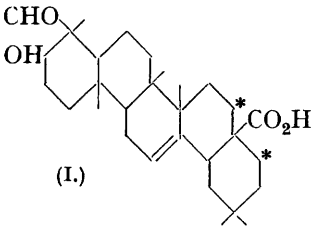
The production of a diketone shows that both hydroxyl groups of quillaic acid must be secondary, since a primary hydroxyl group would undoubtedly have suffered oxidation beyond the aldehyde stage and given rise to an acid $C_{29}H_{42}O_5$.

The diketone does not react with *o*-phenylenediamine or give a colour with ferric chloride; the absorption spectrum of the dinitrophenylhydrazone shows no bands attributable to conjugation (maximum at 3670 A., log $\varepsilon = 4{\cdot}39$). It follows that the second carbonyl group cannot occupy an α- or β-position with respect to the first one and therefore cannot be in ring A. At the same time the spectrum of the diketone is not that of a simple ketone (maximum at 2450 A. in chloroform–alcohol and another at 3240 A. in chloroform, with an inflection at 2560 A.; log $\varepsilon = 2{\cdot}89$, $2{\cdot}91$, and $2{\cdot}98$ respectively) and it would appear that the second carbonyl group is in some way associated with the lactone group; there is at present no chemical evidence of such an arrangement of groups except perhaps the comparatively ready hydrolysis of quillaic ester.

Quillaic acid itself is oxidised by chromic acid to a neutral compound, $C_{29}H_{40}O_5$: both hydroxyl groups are again oxidised to carbonyl groups and ring A undergoes degradation as before, but the inert double bond also is hydroxylated. This is followed by lactone formation and finally oxidation of the remaining hydroxyl group to a carbonyl, which thus occupies a position in ring C :



The formation of this *triketo-lactone* is exactly analogous to that of the keto-lactone $C_{30}H_{46}O_4$ from oleanolic acid (Prelog, *Coll. Czech. Chem. Comm.*, 1930, **2**, 414; 1933, **5**, 165; Kitasato and Sone, *Acta Phytochim.*, 1932, **6**, 179; Ruzicka, Hösli, and Hofmann, *Helv. Chim. Acta*, 1936, **19**, 109). The absorption spectrum of the triketo-lactone is that of a simple ketone (maximum at 3020 A., log $\varepsilon = 2{\cdot}67 \pm 8\%$) and it follows that there can be only one carbonyl group in ring C.



(I.)

From the close similarity in the reactions of quillaic acid and gypsogenin (I) * it appears probable that quillaic acid is a hydroxygypsogenin. Experiments are now in progress with the object of confirming the identity of the carbon skeleton of these two sapogenins; the position of one hydroxyl group is left open for the present, but two possible positions are indicated by asterisks.

Experimental.

(All specimens for analysis were dried for 2 hours at 110°/1—2 mm. unless otherwise stated; m. p.'s are uncorrected.)

Preparation of Quillaic Acid.—Of the numerous experiments performed with a view to

* The carbon skeleton is that originally proposed by Haworth (*Ann. Reports*, 1937, 327 *et seq.*) and lately adopted by Ruzicka and his collaborators.

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improving the preparation of quillaic acid, the following proved the most successful: 50 g. of saponin (manufactured by Messrs. A. Boake Roberts and Co. of Stratford) in 234 c.c. of water were heated and stirred, and 167 c.c. of hydrochloric acid added; the solution was boiled for 7 hours. After the first hour a slimy brick-red precipitate separated, probably the prosapogenin, and this gradually became darker and more granular and finally almost black; it was filtered off and repeatedly boiled with 200 c.c. portions of water until coloured impurities were no longer extracted, then dried at 100° and finally in a vacuum (solid A). This solid was extracted with ether (Soxhlet) and the gelatinous solid obtained on evaporation was collected and washed with a little ether (solid B). It was a sandy powder, m. p. 275°, and therefore did not contain much prosapogenin (m. p. 220°). Four crystallisations from pure ethyl acetate (prepared by Wade's method, J., 1905, **87**, 1656; 1912, **101**, 2429) gave quillaic acid of m. p. 290°.

On a large scale 6 kg. of saponin gave 900 g. of solid A, from which 397 g. of solid B were obtained. A quantity of solid A was also prepared for us by Messrs. A. Boake Roberts and Co.

Numerous methods for the purification of solid B were investigated. The barium salt method successfully used for boswellic acid (Winterstein and Stein, *Z. physiol. Chem.*, 1932, **208**, 9) was unsuccessful because the impurities, evidently acidic, were carried down in the precipitation of the salt; for the same reason reprecipitation from an alkaline solution and Windaus, Hampe, and Rabe's potassium salt method (*loc. cit.*) were ineffective. A better result was achieved by dissolving 10% of solid B in hot alcohol and slowly adding water to the mechanically-stirred solution until separation of solid set in. The first crop was resinous, but presently granular quillaic acid began to appear. The solution was filtered hot at this point and more water was added to the filtrate, precipitating the sapogenin. This method was only used for the purification of very crude sapogenin and did not remove all the colour. The main bulk of the crude material was boiled for about 1 hour in 100 g. portions with 500 c.c. of pure ethyl acetate in a flask fitted with a stirrer and condenser. Only a part of the solid dissolved, but most of the coloured impurities passed into solution; the solid was filtered off and pressed. It was then again recrystallised from ethyl acetate, but to avoid the separation in a gelatinous form, which generally occurred on slow cooling, 50 g. of the material were extracted overnight with 500 c.c. of the solvent in a modified Soxhlet apparatus (compare this vol., p. 1126); the solvent was kept boiling by means of an oil-bath, the level of the oil being about 1 cm. below the level of the solvent to prevent the resinification of the solid which separated in the course of the extraction. The warm extract was rapidly filtered through a sintered glass funnel with large pores, and the solid well pressed and washed with cold ethyl acetate, then with petroleum (yield 150 g., m. p. 287—290°). The mother-liquors gave on evaporation 230 g. of solid contaminated with gummy impurities, which was purified by the partial precipitation method described above. It proved to be mainly prosapogenin (m. p. 210—215°) and was rehydrolysed as described above. The crude sapogenin obtained from it after ether extraction (105 g.) had m. p. 255° and proved difficult to crystallise, but gave a good yield of diacetyl-lactone (40 g.) (see below).

The analytical specimen of quillaic acid was prepared by repeated crystallisation from ethyl acetate and had m. p. 292—293° and $[\alpha]_D$ +56·1° (c = 2·888 in pyridine) (Found: C, 73·9, 74·1, 74·0, 74·1; H, 9·6, 9·4, 9·6, 9·7. $C_{30}H_{46}O_5$ requires C, 74·1; H, 9·5%); a crystalline specimen was also prepared by hydrolysis of diacetylquillaic acid with cold aqueous-alcoholic potassium carbonate, followed by crystallisation from ethyl acetate. Microtitrations of quillaic acid were carried out by the procedure of Ruzicka (*Helv. Chim. Acta*, 1932, **15**, 472), oleanolic acid being used as a standard of comparison; difficulty was experienced because the acid is very weak and the degree of hydrolysis of the sodium salt is considerably affected by the amount of alcohol present (Found: M, 481·8, 485·6, 484·8. Calc., 486·7).

Methyl Ester.—This was prepared in 80% yield by treating a suspension of the acid in "AnalaR" acetone with ethereal diazomethane and recrystallised from methyl alcohol; m. p. 222—223° (Windaus *et al.*, *loc. cit.*, give m. p. 225°), $[\alpha]_D$ +40·5 (c = 4·048 in pyridine); a specimen prepared in ethereal solution did not crystallise (Found: C, 74·2, 74·2; H, 9·9, 9·5. $C_{31}H_{48}O_5$ requires C, 74·4; H, 9·7%). 250 Mg. of the ester were boiled for 5 hours with 10 c.c. of 10% ethyl-alcoholic potassium hydroxide, and the dark yellow solution poured into water and extracted with ether, 80 mg. of ester being recovered; the aqueous layer yielded 150 mg. of an amorphous acid, m. p. 287—290°, on acidification. An attempt to reduce the ester with aluminium *iso*propoxide led to an uncrystallisable gum.

Diacetyl-lactone.—An ice-cold solution of 1 g. of quillaic acid in 10 c.c. of acetic acid was saturated with dry hydrogen bromide, a few drops of acetic anhydride added, and the deep

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red solution poured into water after 3 days. The solid was dissolved in ether–chloroform, and the solution shaken with 10% aqueous sodium hydroxide (this is only necessary when crude quillaic acid is employed and generally leads to some loss owing to the ready deacetylation of the lactone), dried over sodium sulphate, and evaporated. The resulting red gum was dissolved in the minimum quantity of hot chloroform, and methyl alcohol added until crystals began to appear, 350 mg. of *diacetyl-lactone* being obtained in fine needles, m. p. 260° with previous softening. The yield was increased to 500 mg. by previous acetylation of the sapogenin. Hydrogen chloride can be used in place of the bromide, but gives a poorer yield of lactone unless zinc chloride is added to the mixture; zinc chloride does not, however, improve the yield when hydrogen bromide is used. For analysis the lactone was crystallised six times from chloroform–methyl alcohol and had $[\alpha]_D$ −21·5° (c = 3·348 in chloroform) (Found: C, 71·3, 71·7; H, 8·6, 8·9. $C_{34}H_{50}O_7$ requires C, 71·5; H, 8·9%).

Quillaic Lactone.—This compound occurs in the mother-liquors from the preparation of the diacetyl-lactone and can be readily prepared by alkaline hydrolysis of the latter. It forms small iridescent plates, m. p. 315°, from chloroform–methyl alcohol; neither it nor the preceding compound gives a colour with tetranitromethane (Found: C, 73·8; H, 9·2. $C_{30}H_{46}O_5$ requires C, 74·1; H, 9·5%).

Oxidation of the Diacetyl-lactone.—A solution of 10 g. of the diacetyl-lactone in 500 c.c. of acetic acid was mechanically stirred and kept at 20—25° while a solution of 3·6 g. of chromic acid and 3 c.c. of sulphuric acid in 180 c.c. of acetic acid were dropped in (5 hours), the addition being more rapid towards the end. The excess of reagent was destroyed with methyl alcohol, the acetic acid distilled off under reduced pressure, the residue extracted with ether, and the ethereal solution extracted with ice-cold 10% aqueous sodium hydroxide. The extract was acidified, and the precipitate filtered off, washed, and dried (8 g.). The crude acid was dissolved in the minimum amount of hot methyl alcohol, and the solution cooled and scratched; after about 12 hours long silky needles of the acetyl *acid* began to separate (2 g.) and were recrystallised from methyl alcohol; they softened at 204°, then resolidified and melted at 278—280°. The acid was freely soluble in ether, methyl and ethyl alcohol and very soluble in chloroform and was saturated to tetranitromethane (Found: C, 69·3, 69·4; H, 8·9, 8·9. $C_{34}H_{50}O_8$ requires C, 69·6; H, 8·6%). In preliminary experiments it was found that, if less chromic acid is used than is required to give 3 atoms of oxygen, some diacetyl-lactone remains unattacked. When potassium hydroxide was used in the extraction of the acid reaction product, the latter suffered deacetylation and the *acid* $C_{30}H_{46}O_6$ was produced (150 mg. from 1 g. of diacetyl-lactone); it crystallised from methyl alcohol in silky needles, m. p. 380° (Found: C, 71·3, 71·2; H, 9·0, 8·9. $C_{30}H_{46}O_6$ requires C, 71·7; H, 9·2%). The same acid was produced when 8 g. of the crude acetyl acid in 50 c.c. of alcohol were warmed and shaken with 30 c.c. of 10% ethyl-alcoholic potassium hydroxide until the precipitate of potassium salt had redissolved. After ½ hour the solution was acidified and poured into water, 6·8 g. of crude acid being obtained, and this gave 4 g. of pure acid.

The C_{30} acid was recovered (after acidification) unchanged after being boiled for 3 hours with 10% alcoholic potassium hydroxide; it is evidently impossible to isolate the hydroxy-acid formed by the opening of the lactone ring, just as in the case of hederagenin lactone (Winterstein and Meyer, *Z. physiol. Chem.*, 1931, **199**, 37). The acid was readily esterified with diazomethane in acetone–ether; the *ester* crystallised from chloroform in flat, silky needles which become opaque on drying, m. p. 375° (Found: C, 72·0, 72·1, 71·9; H, 9·5, 9·4, 9·5. $C_{31}H_{48}O_6$ requires C, 72·1; H, 9·4%). 200 Mg. of the ester were boiled for 3 hours with 10 c.c. of 5% alcoholic potassium hydroxide; 120 mg. of unchanged ester were recovered, together with 75 mg. of the acid. The slow rate of hydrolysis is analogous to the behaviour of gypsogeninic ester (Ruzicka, Giacomello, and Grob, *loc. cit.*) and suggests that the newly-formed carboxyl group is attached to a quaternary carbon atom.

Oxidation of the C_{30} Acid.—5 G. of the finely powdered acid, suspended in 500 c.c. of acetic acid, were mechanically stirred at 20° while a solution of 3 g. of chromic acid in 300 c.c. of acetic acid was dropped in during 7 hours. After the excess of reagent had been destroyed with methyl alcohol, the acetic acid was distilled off under reduced pressure, the solid residue dissolved in ether–chloroform, and the solution extracted with 10% aqueous sodium hydroxide. The solution in the organic solvents was freed from traces of chromium salts by shaking with hydrochloric acid and then with brine, dried, and evaporated, 2·3 g. of solid residue being obtained; the alkaline extract gave 1·95 g. of crude acid on acidification. The neutral portion crystallised in some experiments, but it was found preferable to purify it by chromatographic adsorption. It was dissolved in 115 c.c. of benzene and passed through a column of 50 g. of

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activated alumina, which was then washed with benzene. The solution was collected in three approximately equal fractions, the first two of which gave the same compound on evaporation; the third contained no crystalline material. The solid obtained from the first two fractions was recrystallised from ethyl acetate containing a little chloroform; it formed small plates, m. p. 296—297°, sparingly soluble in methyl or ethyl alcohol, freely soluble in acetic acid, $[\alpha]_D$ — 83·5° (c = 2·096 in chloroform) (Found: C, 76·9, 76·7; H, 9·5, 9·5. $C_{29}H_{42}O_4$ requires C, 76·6; H, 9·3%). It contained no active hydrogen and gave no colour with tetranitromethane or with alcoholic ferric chloride. The *semicarbazone* crystallised from acetic acid in fine needles, m. p. 301—302° (Found: C, 70·4, 70·3; H, 8·9, 8·7. $C_{30}H_{45}O_4N_3$ requires C, 70·4; H, 8·9%). The 2 : 4-*dinitrophenylhydrazone* separated from acetic acid in minute yellow needles, m. p. 298—299° (Found: C, 66·2; H, 7·3; N, 8·7. $C_{35}H_{46}O_7N_4$ requires C, 66·2; H, 7·3; N, 8·8%). An oxime was also prepared but could not be made to crystallise; the ketone did not form a quinoxaline on boiling with *o*-phenylenediamine in alcohol for an hour. An attempt to reduce it by Clemmensen's method led to an uncrystallisable gum.

The acidic portion of the oxidation product was dissolved in a little methyl alcohol. On keeping in a refrigerator a small crop of crystals (A) was deposited; the mother-liquor yielded a much larger crop (B) (400 mg.). The solid (A) was again recrystallised from methyl alcohol; a crop of plates (A_1), m. p. 310—312°, was obtained, and from the mother-liquor of it plates (A_2), m. p. 320°, mixed m. p. with (A_1) 315—316° [Found for (A_1): C, 70·1, 70·2; H, 8·7, 8·7; for (A_2): C, 71·3, 71·2; H, 8·9, 8·9%]. The acid (B) was much less soluble in ethyl acetate than the acids (A_1) and (A_2) and it was recrystallised from this solvent and then from methyl alcohol; it formed long needles, m. p. 290—291° (Found: C, 69·9, 70·0, 70·0; H, 9·0, 9·0, 9·0%; *M*, by titration, 493, 504). It did not react with semicarbazide and had no selective absorption in ultra-violet light. The *methyl* ester, prepared with diazomethane, crystallised from methyl alcohol in stout needles, m. p. 206° (Found: C, 70·5; 70·3; H, 9·3, 9·4%). The analysis figures agree well with those required for an acid $C_{22}H_{34}O_5$ (Calc.: C, 69·8; H, 9·1%) and its ester $C_{23}H_{36}O_5$ (Calc.: C, 70·4; H, 9·3%), but this formula is not consistent with the results of titration and the formation of the acid appears difficult to explain. The ester was completely hydrolysed by boiling for 3 hours with 5% alcoholic potassium hydroxide, showing that the carboxyl group which had been esterified is not attached to a quaternary carbon atom, as in the C_{30} acid, and must have resulted from the opening of a ring.

Oxidation of Quillaic Acid.—A solution of 5 g. of the acid in 200 c.c. of acetic acid was mechanically stirred and cooled in ice-water while a solution of 7·5 g. of chromic acid and 6·5 c.c. of sulphuric acid in 375 c.c. of acetic acid and 20 c.c. of water was run in during 3 hours. The stirring was continued for a further hour, and the solution worked up as described on p. 1133. The acid portion did not crystallise and was set aside. The neutral portion was a yellow gum, which was chromatographed in benzene solution, and a portion which was more strongly adsorbed kept separate. The main bulk separated from ethyl acetate as an almost colourless solid, m. p. 256—260°, which was dried at 110°/0·0006 mm. (Found: C, 74·1; H, 8·9. $C_{29}H_{40}O_5$ requires C, 74·3; H, 8·6%); a minute amount of a pseudo-acidic gum was also isolated.

Dihydroquillaic Acid.—2 G. of quillaic acid in 100 c.c. of acetic acid were shaken with 0·3 g. of Adams's catalyst in an atmosphere of hydrogen for 18 hours, 86 c.c. of hydrogen being absorbed. The filtered solution was evaporated under reduced pressure, and the residue crystallised from methyl alcohol, then from ethyl acetate (Soxhlet); it formed silky needles, m. p. 315—316°, freely soluble in hot acetic acid, sparingly so in methyl alcohol; it gave a yellow colour with tetranitromethane and had $[\alpha]_D$ +32° (c = 1·836) in pyridine (Found: C, 73·9; H, 10·0. $C_{30}H_{48}O_5$ requires C, 73·7; H, 10·0). On a larger scale less catalyst was used and a 75% yield of the *dihydro-acid* was obtained. The *methyl* ester was prepared with the aid of diazomethane in acetone in somewhat poor yield and formed plates, m. p. 269—270°, from methyl alcohol–benzene, which were dried at 85°/0·002 mm. for 12 hours (Found: C, 74·3; H, 10·2. $C_{31}H_{50}O_5$ requires C, 74·1; H, 10·0%).

Acetonyl Derivative of the Methyl Ester.—The crude methyl ester (2·3 g.), dissolved in the minimum amount of dry acetone, was treated with 5 drops of concentrated hydrochloric acid, and the solution warmed for a few minutes and kept in the refrigerator for 3 weeks; a small amount of crystalline solid separated, m. p. 256—259° (Found: C, 75·5; H, 10·1. $C_{34}H_{54}O_5$ requires C, 75·2; H, 10·0%).

Triacetyl-lactone.—Dihydroquillaic acid was acetylated with acetic anhydride and pyridine in the cold. The acetyl derivative proved difficult to purify, as it was readily deacetylated on boiling with solvents. The crude compound was therefore lactonised as described on p. 1132, and the resulting solid crystallised from methyl alcohol containing a little chloroform (norit);

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it formed fine needles, m. p. 247—249°, and gave no colour with tetranitromethane (Found : C, 70·3; H, 9·0. $C_{34}H_{52}O_7$ requires C, 70·3; H, 8·9%).

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