133. *Sapogenins. Part IX. The Occurrence and Constitution of Bassic Acid.*

By B. Jason Heywood and George A. R. Kon.

Bassic acid (Heywood, Kon, and Ware, J., **1939**, 1124) has been isolated from the seeds of all except two of the *Sapotaceæ* which we have examined, and appears to be the characteristic sapogenin of this order.

The position of one primary and one secondary hydroxyl group in bassic acid has already been demonstrated; it is now shown that the third hydroxyl is secondary and occupies a position β with respect to the other secondary hydroxyl group. It must therefore be placed on C_4 in ring *A*. Evidence is also adduced for placing one of the double bonds of bassic acid in ring *B* between C_6 and C_7 and a complete formula (IX) is suggested, in which the positions of the carboxyl group and of the second double bond, which is in a position βγ or γδ with respect to it, are assumed by analogy with other triterpenes and still require proof.

In Part V (*loc. cit.*) it was concluded that the sapogenin bassic acid, which had been isolated from three species of *Bassia*, has a pentacyclic skeleton similar to that of other triterpenes and that two of its three hydroxyl groups are disposed like those of hederagenin. It was shown that there are two double bonds of unequal reactivity and that one of these occupies the usual position βγ or γδ with respect to the carboxyl group, thus accounting for the ready formation of lactones.

It was left to be decided whether bassic acid is identical with an acid isolated by van der Haar from both *Mimusops elengi* L. and *Achras sapota* L. (*Rec. Trav. chim.*, 1929, **48**, 1155, 1166) and formulated as $C_{29}H_{44}O_5$. *M. elengi* seed has now been found to be an excellent source of the sapogenin, which is easily obtained from it in a pure state. It was identified as bassic acid by direct comparison and by the preparation of the methyl ester and especially of the acetonyl derivative of the latter; this constitutes the most certain method for the identification of bassic acid.

The crude saponin content of *Achras sapota* seed of West Indian origin appeared to be normal, but we were unable to prepare from it more than a very small amount of the sapogenin, which was identified as bassic acid; van der Haar worked with seed of Asiatic origin, which evidently yields more sapogenin. There are indications that the sapogenin obtained from *Achras sapota* seed contains another constituent in addition to bassic acid, because a small amount of an ester of higher melting point (233°) was isolated when the sapogenin was esterified and the ester subjected to chromatographic analysis; the amount obtained did not permit further examination.

We have also prepared and examined the sapogenin from a number of other plants of the order *Sapotaceæ*, namely, *Bassia longifolia* L. (= *Madhuca longifolia* Roxb.) from Ceylon and from Burma, *Mimusops hexandra* Roxb. from Ceylon, *M. djave* Engl. from Nigeria, *Dumoria Heckelii* Pierre from the Gold Coast, *Payena lucida* DC. and *Palaquium gutta* Burck. from the Federated Malay States and " ketiau nuts " (*Palaquium sp.*) * from N. Borneo. With the exception of the last two, which did not give a pure sapogenin, these seeds yielded varying amounts of bassic acid, which evidently occurs in a large number of *Sapotaceæ* and appears to be characteristic of them.

In the course of this work we were able to clear up certain discrepancies in the properties of the sapogenin and some of its derivatives, for it appears that the acid sometimes separates in a hydrated form or with alcohol of crystallisation, but when pure tends to separate without solvent of crystallisation, although the last traces of the latter are tenaciously retained. Also, the alcohol-containing crystals first obtained tend to lose their solvent of crystallisation on keeping.†

The methyl ester of bassic acid occurs in two forms, the α of m. p. 214—215°, $[\alpha]_D + 64°$,

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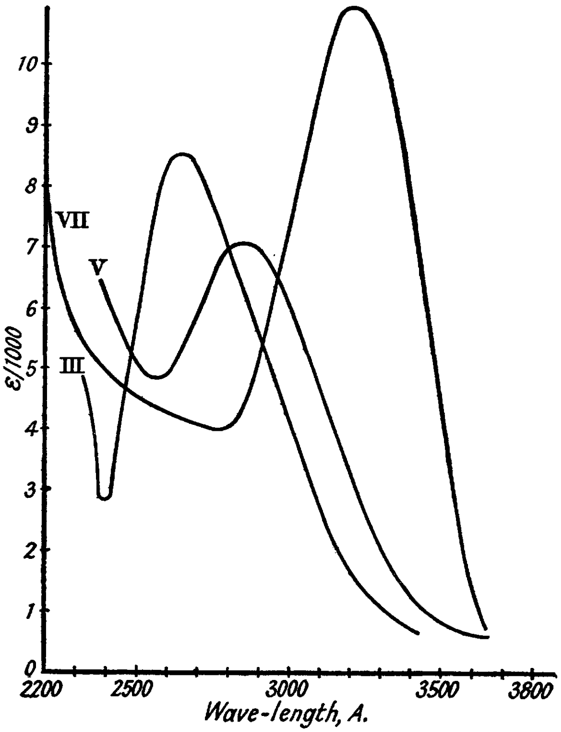
* Wehmer (" Die Pflanzenstoffe," Jena, 1931) mentions two plants as producing Katiau or Ketiauw oil, namely, *Bassia mottleyana* Clarke and *Payena bankensis* Burck.

† This is doubtless the reason for the variations in the rotation of the acid which are sometimes observed.

and the β, m. p. 220°, $[\alpha]_D$ + 55·5°. Both give the same acetonyl derivative, from which the α-form is generally regenerated in methyl-alcoholic solution and the β-form in ethyl alcohol. A mixture of the two forms exhibits a marked depression of the melting point. They may be distinguished by the ability of the α-form to crystallise from benzene, from which the β-isomeride separates in a gelatinous condition; it does, however, crystallise extremely well from methyl or ethyl alcohol. Again, the β-ester gives rise without difficulty to the crystalline triacetate already prepared by van der Haar (*loc. cit.*), whereas the acetate of the α-ester is only obtained with difficulty and does not separate from solvents in a crystalline condition.

Only the α-ester undergoes catalytic hydrogenation, but this often fails for no apparent reason and the investigation of the dihydro-derivative has not yet been completed. The statement that one double bond of bassic acid is much more reactive than the other (Heywood, Kon, and Ware, *loc. cit.*) may therefore require qualification.



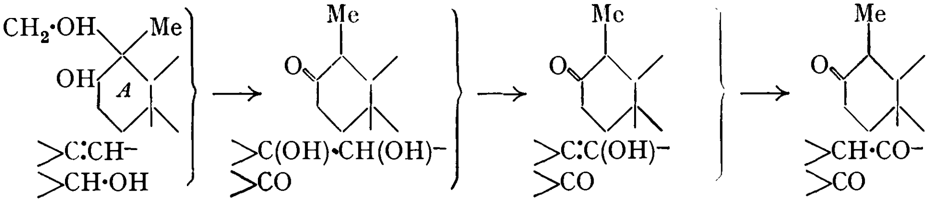
As the outcome of the experiments described below, it has been possible to ascertain the position of one of these double bonds and of the last remaining hydroxyl group, in spite of the fact that most of the standard methods of oxidative degradation led to uncrystallisable products; for example, all attempts to oxidise the acid or its ester with chromic acid or permanganate were uniformly unsuccessful. Other negative results include the oxidation of the ester with lead tetra-acetate and with periodic acid, from which it can be concluded that the acid does not contain an α-glycol grouping. The ester was recovered unchanged after prolonged treatment with Oppenauer's reagent.

We were more successful with the acetonyl derivative of the ester, in which a primary and a secondary hydroxyl group in the 1 : 3-position to one another are protected. The third hydroxyl is oxidised by chromic acid and a new *acetonyl* derivative is formed, which can be hydrolysed to the parent ketonic *ester*; this forms a *semicarbazone*. The new acetonyl compound has no reducing properties and resists further oxidation; the hydroxyl group which has undergone oxidation must therefore have been a secondary, and not a primary one.

Evidence regarding the position of this group and also of one double bond is afforded by the reactions of the bromo-lactone of bassic acid, in which the other double bond is protected by lactonisation. Like other bromo-lactones derived from triterpene acids, this compound can be reconverted into the parent acid by treatment with zinc and acetic acid and it forms a (?) *hydroxy-lactone* with alkali (compare Kitasato and Sone, *Acta Phytochim.*, 1932, **6**, 179).

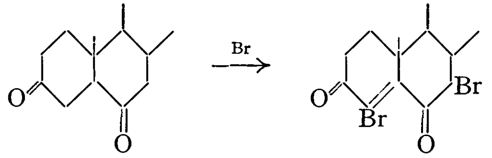
Oxidation of the bromo-lactone $C_{30}H_{45}O_5Br$ with chromic acid gives a crystalline solid, $C_{29}H_{39}O_5Br$, which was at first thought to be a weak acid, but was later recognised as a strongly acidic diketone, giving an intense purple colour with ferric chloride and forming a yellow potassio-derivative; the carbonyl groups responsible for enolisation must be in the β-position to one another, since an α-diketone is not likely to survive the conditions under which the compound is formed and for other reasons which are discussed below. This formulation is borne out by the absorption spectrum of the diketone (Figure), which shows a band with a maximum at 2640 A. (log $\varepsilon_{max.}$ = 3·93) and is thus comparable with that of cholestane-2 : 3-dione, the two enol forms of which have bands at 2700 and 2720 respectively (log $\varepsilon_{max.}$ 3·70 and 3·93) (Rosenheim and Stiller, J., 1938, 353); similarly, the acetate of cholestan-3-ol-6 : 7-dione has a band at 2745 A. (log $\varepsilon_{max.}$ = 4·03) (Heilbron, Jones, and Spring, J., 1937, 801). Unpublished observations made in these laboratories show that enolised cyclic α- and β-diketones show similar absorption, except that the maxima for α-diketones are somewhat nearer the visible part of the spectrum.

Now in the formation of the diketone from the bromo-lactone the grouping $-CH(OH)\cdot CMe\cdot CH_2\cdot OH$ is oxidised to $-CO\cdot CHMe$ as in the degradation of hederagenin to hedragone, and the remaining secondary hydroxyl group is converted into carbonyl, thus accounting for the loss of a carbon atom, six hydrogen atoms and an oxygen atom; a new oxygen atom is therefore introduced without the elimination of hydrogen atoms. This evidently takes place by the hydroxylation of the double bond and subsequent elimination of water, as in the oxidation of nor-β-boswellenone to nor-β-boswellanedione (Simpson and Williams, J., 1938, 1712) and in many other examples:

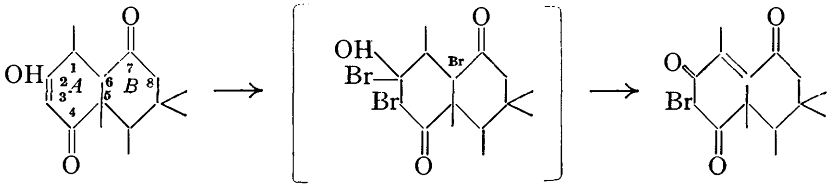


The new carbonyl group appears to be inert and does not react with the usual carbonyl reagents: for instance, the triketone only forms a *mono-2 : 4-dinitrophenylhydrazone.* There is evidence, however, both of the ketonic nature of this group and of its position in the molecule δ with respect to another carbonyl group. On treatment with bromine the triketone loses two hydrogen atoms with great ease and a bromine atom is also introduced by substitution. Such a dehydrogenating action of bromine has been noted in ketones derived from both α- and β-amyrin and gives rise to αβ-unsaturated ketones (Seymour, Sharples, and Spring, J., 1939, 1075; Picard, Sharples, and Spring, *ibid.*, p. 1045), and an exact parallel is provided by the bromination of cholestane-3 : 6-dione (I) to the unsaturated dibromide (II) (Butenandt, Schramm, and Kudszus, *Annalen*, 1937, **531**, 176); in our case, however, the carbon atom C_1 is already fully substituted and only one atom of bromine is introduced instead of two, the process being represented by formulæ (III) to (V):

(I.)



(II.)



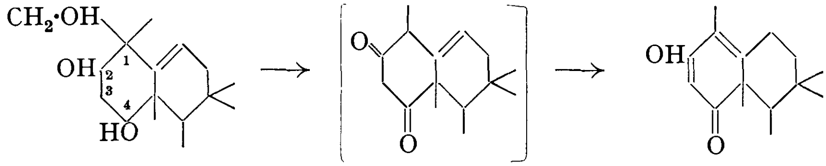
(III.) (IV.) (V.)

Of the two possible positions for the bromine atom, C_3 and C_8, we favour the former because the new triketone is no longer enolised; it also possesses a marked yellow colour. The absorption spectrum of the dibromo-triketone (V) has a band at 2840 A. (log $\varepsilon_{max.}$ = 3·86). This is much nearer the visible region than would be expected by analogy with Δ^4-cholestene-3 : 6-dione or its dibromide (II), both of which absorb at about 2520 A. (Butenandt, Schramm, and Kudszus, *loc. cit.*); we are at present unable to explain this difference.

From the reactions described above, it can be concluded that the third hydroxyl group of bassic acid must be situated on C_4 in ring *A*,* and that the double bond which does not take part in lactone formation must be accommodated in ring *B*, between C_6 and C_7.

These conclusions receive decisive confirmation from a re-examination of the diketone previously obtained by the oxidation of bassic ester with copper bronze. We were again unsuccessful in our attempts to prepare the diketone in a crystalline condition; it has, however, been obtained analytically pure and the formula $C_{30}H_{42}O_4$ (erroneously given as $C_{30}H_{44}O_4$ by Heywood, Kon, and Ware, *loc. cit.*, p. 1125) confirmed. The pure compound gives an intense colour with ferric chloride, dissolves in alkali, and has one active hydrogen atom (Zerevitinov); it is therefore an enol. In its formation no additional oxygen atom has been introduced, as in the formation of the triketone (III), and it is clear that the two carbonyl groups must represent the two secondary hydroxyl groups of bassic acid. Since the acid does not contain the α-glycol grouping (p. 714) and the diketone is not oxidised by alkaline hydrogen peroxide, these carbonyl groups must be in the β-position to one another, as already suggested.

The absorption spectrum of the diketone shown in the figure differs sharply from those of the two triketones. There is a strong band at 3230 A. (log $\varepsilon_{max.} = 4{\cdot}04$), which cannot be accounted for merely by the enol form of the diketone; it is, however, consistent with a structure containing a carbonyl group conjugated with *two* double bonds, both of the latter being situated in the same ring (compare, for example, 6-keto-3-acetoxy-$\Delta^{2:4}$-cholestadiene; Heilbron, Jackson, Jones, and Spring, J., 1938, 102). To form such a system it is necessary for another double bond to become conjugated with the double bond formed by the enolisation of one of the carbonyl groups (on C_2). This can be readily brought about by the wandering of the double bond placed in ring *B* after the elimination of the primary carbinol group:



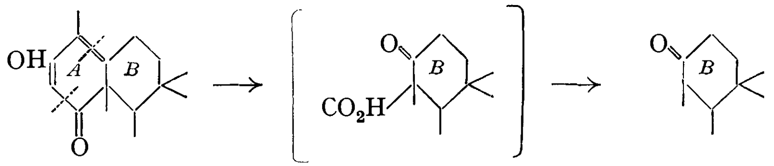
(VI.) (VII.)

The change is thus exactly analogous to the formation of cholestenone from cholesterol and is, incidentally, caused by the same oxidising agent (compare Sexton, J., 1928, 2825).

The spectrum of the 2 : 4-dinitrophenylhydrazone of (VII) suggests a singly conjugated system (*loc. cit.*); this appears to be due to the fact that the carbonyl group on C_2 reacts in preference to that on C_4 and the compound is therefore a derivative of the diketonic form, in which only one double bond is conjugated with the more reactive carbonyl group.

Quantitative microhydrogenation of the diketone (VII) leads to the addition of 5·8 atoms of hydrogen; on a preparative scale, however, a crystalline *tetrahydro*-derivative, $C_{30}H_{46}O_4$, is readily obtained. This is still unsaturated to tetranitromethane and forms a 2 : 4-dinitrophenylhydrazone, but it no longer has the system of conjugated double bonds characteristic of the diketone (VII); its absorption spectrum shows a band of low intensity in the region of 2800 A. ($\varepsilon = 15$—20) attributable to a saturated ketone. It is therefore the hydroxyketone corresponding to (VII), but fully saturated in ring *A*. The ready hydrogenation of the double bonds in ring *A* is in marked contrast with the difficulty experienced in hydrogenating the double bond in ring *B* before the isomeric change involved in the formation of the dione (VII).

The oxidation of the dione might be expected to give rise to a neutral ketone (VIII) by way of an unstable β-ketonic acid, with the complete destruction of ring *A* (compare Inhoffen, *Ber.*, 1939, **72**, 1686):



(VIII.)

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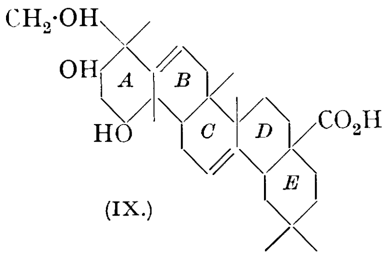
* It is obvious that these hydroxyl groups can only be accommodated in one of the terminal rings.

The action of chromic acid does, indeed, lead to a neutral ketone, but this is unfortunately amorphous and its 2 : 4-*dinitrophenylhydrazone* is also somewhat indefinite in appearance. This compound gives analytical figures in better agreement with a formula containing two hydrogen atoms less than would be expected and has a bright scarlet colour; its constitution therefore requires further proof.

Further experiments are in progress with the object, in particular, of securing decisive evidence regarding the position of the carboxyl group of bassic acid together with that of the remaining double bond, which takes part in lactone formation. For the present it seems justified to assume that they occupy the same respective positions as the carboxyl and the double bond of the β-amyrin group of triterpenes (hederagenin), in which case bassic acid can be formulated as (IX).



(IX.)

The position of the second double bond of bassic acid in ring *B* is one of the two positions which have been put forward for the double bond of β-boswellic acid (Simpson and Williams, *loc. cit.*). This acid has been converted into α-amyrin (Ruzicka and Wirz, *Helv. Chim. Acta*, 1939, **22**, 948) and it appears possible that such a position of the double bond is characteristic of the α-amyrin group of triterpenes. Bassic acid would, in that case, occupy an interesting intermediate position as a member of both groups.

EXPERIMENTAL.

The melting points are uncorrected. Unless otherwise stated, specimens for analysis were dried for 2 hours at 100°/1 mm.

Extraction of Bassic Acid.—The extraction of bassic acid from the seeds of various *Sapotaceæ* was carried out as described by Heywood, Kon, and Ware (*loc. cit.*) and the results are summarised in Table I.

TABLE I.

Source.	Kernel in nut, %.	Fat in kernel, %.	Crude saponin in fat-free meal, %.*	Sapogenin, % on fat-free meal.	Acid, m. p.	$[\alpha]_D$ in pyridine.	Ester, m. p.	$[\alpha]_D$ in chloroform.	Acetonyl derivative, m. p. and mixed m. p.
B. latifolia	—	47	26	1·8	316°	+82·9°	213°	+63°	205°
B. longifolia (Burma) ...	75	51	39	3·3	317—318	+82·6	217 (β)	+56·8	205—206
B. longifolia (Ceylon) ...	78	58	50	4·8	316	+82·9	216—217 (β)	+56·2	205—206
B. butyracea	75	60	27	2·8	316	+82·4	210—212	+64	205—206
B. Parkii	62	43	23	0·23	309	+82·4	211—212	+63·6	205—206
A. sapota	45	25	20	0·07	329	—	216—217 (β)	—	205—206
M. hexandra	46	40	22	1·23	306—309	+83·3	218—219 (β)	—	205—206
M. elengi	37	23	50	2·4	309—310	+85·7	219 (β)	+55·5	205—206
M. djave	64	49	35	0·58	314—316	+76	213	—	205—206
D. Heckelii	38	53	47	0·41	316	+77	215 (β)	+55·5	205—206
P. lucida	70	6	67	1·0	319—320	+84·1	219 (β)	+56·1	205
P. gutta	80	57	28	No pure sapogenin was obtained					
P. Sp.	75	56	9	,,	,,	,,	,,		

* This figure includes sugars; the amount of these was insignificant except in the case of *P. lucida*, from which 32% of crystalline sugar was isolated.

The highest yield of sapogenin, amounting to 4·8% calculated on the fat-free meal, was obtained from *B. longifolia* (from Ceylon) and this is distinctly higher than the best yield previously recorded (from *B. butyracea*); the yield naturally depends on the condition of the seed, absence of mould, etc. The sapogenin is also obtained with great ease from the seed of *M. elengi*, but this is only available in small amounts. *M. hexandra* seed, the source of Rayan oil (compare Patel, *J. Indian Inst. Sci.*, 1925, **7**, 71), is inconveniently small (25 seed kernels to 1 g. on the average) and consequently difficult to shell.

Methyl Bassate, β-Form.—This has evidently been prepared by van der Haar (*loc. cit.*), who did not, however, realise the difference between the two esters (Found for a specimen prepared from *M. elengi* : C, 74·3; H, 9·6. $C_{31}H_{48}O_5$ requires C, 74·4; H, 9·7%). The acetonyl compound prepared from it had m. p. 205—206° (Found : C, 75·2; H, 9·5. Calc. : C, 75·5; H, 9·7%).

Methyl Triacetylbassate.—This was prepared from the β-ester as described by van der Haar (*loc. cit.*) and had m. p. 148—149° (Found : C, 71·0; H, 8·8. Calc. : C, 70·9; H, 8·7%).

Methyl Dehydrobassate.—2·2 G. of the finely ground acetonyl derivative of bassic ester, suspended in 110 c.c. of "AnalaR" acetic acid, were mechanically stirred at 0—10° while 0·5 g.

of chromic acid in 15 c.c. of acetic acid was added dropwise during 1¼ hours. The excess of reagent was decomposed with sodium sulphite, and the solution poured into 750 c.c. of water. The solid was washed with 10% sodium hydroxide solution and crystallised from acetone containing a little hydrochloric acid; 1·05 g. of plates, m. p. 178—182°, were obtained. In another experiment 4·4 g. of starting material gave 1·75 g. of product, m. p. 183—185°. A solution of this in benzene (50 c.c.) was percolated through 15 g. of activated alumina, followed by 50 c.c. of benzene, then 100 c.c. of benzene containing 1% of methyl alcohol. The first 50 c.c. of solution gave 1 g. of solid, m. p. 181—183°, on evaporation and crystallisation of the residue from acetone; the second 50 c.c. gave similar material, and the last runnings contained unchanged starting material, m. p. 203—205°. The new *acetonyl* compound formed large transparent prisms, m. p. 181—183°, not depressed by the acetonyl compound of bassic ester (Found : C, 75·8; H, 9·5. $C_{34}H_{50}O_5$ requires C, 75·8; H, 9·4%).

The acetonyl compound was boiled with alcohol containing a little hydrochloric acid until all the solid had gone into solution, which was then gradually diluted with water until a slight turbidity appeared. Crystals soon began to separate, but some gelatinous material was also deposited. The product was therefore precipitated with water and extracted with ether. After removal of the solvent the residue was crystallised from benzene–petroleum, then from benzene and finally from methyl alcohol, forming needles, m. p. 202—203·5° (Found : C, 74·8; H, 9·5. $C_{31}H_{46}O_5$ requires C, 74·6; H, 9·3%). The *ester* formed a canary-yellow precipitate with 2 : 4-dinitrophenylhydrazine. A *semicarbazone* was obtained by dissolving the ester (1·55 g.) in a solution prepared by grinding 1·1 g. of semicarbazide hydrochloride and 1·6 g. of sodium acetate with 15 c.c. of methyl alcohol and filtering the liquid; the crystals that appeared after 3 hours were collected the next day (1·4 g.) and twice recrystallised from methyl alcohol, forming feathery needles, m. p. 210—213° (Found : N, 7·5. $C_{32}H_{49}O_5N_3$ requires N, 7·6%). The diacetate prepared by boiling the ester with acetic anhydride for an hour formed plates, m. p. 88—91°, from dilute acetic acid; it did not give satisfactory figures on analysis.

Conversion of the Bromo-lactone into Bassic Acid.—The bromo-lactone was prepared as described before (*loc. cit.*); it had $[\alpha]_D + 64·8°$ ($c = 2·05$ in chloroform). It formed an *acetonyl* compound, prisms from acetone, m. p. 205—206° (Found: C, 65·6; H, 8·2. $C_{33}H_{49}O_5Br$ requires C, 65·6; H, 8·2%).

900 Mg. of the bromo-lactone in 35 c.c. of acetic acid were heated on the steam-bath, and 5 g. of zinc dust added in small portions in the course of ½ hour with constant shaking. The mixture was heated for a further ½ hour and filtered, and the cake of zinc extracted with acetic acid. The acetic acid solution was diluted with water, and the solid dissolved in ether, from which bassic acid was extracted with 10% potassium hydroxide solution in the form of the sparingly soluble potassium salt. This was filtered off, and the acid liberated and recrystallised from methyl alcohol (650 mg.), m. p. 319—324°; it was identified by a mixed m. p. determination. The rotation of the acid in pyridine solution was rather low ($[\alpha]_D + 72°$), but the compound was esterified and the ester converted into the characteristic acetonyl derivative, which was identified in the usual way.

(?) *Hydroxy-lactone.*—1 G. of the bromo-lactone was boiled for 1½ hours with 2 g. of potassium hydroxide in 30 c.c. of methyl alcohol; another 2 g. of potassium hydroxide were then added, and the heating continued for a further 1½ hours; potassium bromide had then separated. Water was added and the products were extracted with ether after acidification. Very little acidic material was recovered by extraction with alkali; the neutral material left after the evaporation of the ether was repeatedly crystallised from dilute methyl alcohol, forming needles, m. p. 236°; on occasion the m. p. was as low as 215°. From the analytical results it appears that the compound is the lactone and not the methyl ester, which should have been produced by analogy with the corresponding derivative of hederagenin (Kitasato and Sone, *loc. cit.*) (Found : C, 71·6, 71·3; H, 9·2, 9·2. $C_{30}H_{46}O_6$ requires C, 71·7; H, 9·2%).

Oxidation of the Bromo-lactone.—12 G. of the bromo-lactone in 800 c.c. of acetic acid and 80 c.c. of water were mechanically stirred at 5—10° while 8 g. of chromic acid in 250 c.c. of acetic acid were dropped in. As no oxidation took place at first, 6·5 c.c. of sulphuric acid diluted with acetic acid were added; the oxidising agent was then rapidly reduced and the oxidation proceeded normally (on a small scale the addition of sulphuric acid had not been found necessary). The excess of reagent was destroyed with sodium sulphite, and the solvent distilled off under reduced pressure. The residue was treated with water and the products were extracted with ether, the extract being shaken with water and with dilute sulphuric acid. Acidic products were removed by shaking with sodium carbonate solution and the extract was then shaken with 10% potassium hydroxide solution. This caused the precipitation of a yellow potassio-derivative, which was filtered off and decomposed with mineral acid in presence of ether. The ethereal solution gave on evaporation a gum, which solidified on rubbing with methyl alcohol and keeping overnight. It was finally crystallised three times from acetic acid, forming small needles, m. p. 245° (decomp.); the *triketone* (III) was very sparingly soluble in organic solvents except chloroform (Found : C, 63·4, 64·0; H, 6·9, 7·1. $C_{29}H_{39}O_5Br$ requires C, 63·6; H, 7·2%). The 2 : 4-*dinitrophenylhydrazone* was a sparingly soluble, yellow powder, m. p. 286—288° (decomp.) (Found : C, 57·7; H, 5·8. $C_{35}H_{43}O_8N_4Br$ requires C, 57·8; H, 6·0%). The triketone gave on treatment with diazomethane a methyl ether, which could not be crystallised; the 2 : 4-*dinitrophenyhydrazone* of it had m. p. 294—295° (decomp.) (Found : C, 58·0; H, 6·1. $C_{36}H_{45}O_8N_4Br$ requires C, 58·3; H, 6·1%). The absorption of light by this compound in chloroform showed a maximum at 4150 A. with subsidiary maxima at 3130 and 2600 A. (log $\varepsilon_{max.}$ 4·58, 3·78, and 4·25 respectively), suggesting the presence of two conjugated double bonds.

Dibromo-triketone (V).—200 Mg. of the triketone (III) were dissolved in 50 c.c. of boiling acetic acid, and the solution rapidly cooled to obtain the solid in a fine state of division. 5 C.c. of water and 1 g. of sodium carbonate were cautiously added to the ice-cold solution, followed by 50 mg. of bromine in a little acetic acid. The yellow precipitate was collected after an hour and dissolved in chloroform, and the solution shaken with 10% aqueous potassium hydroxide, which did not remove any acidic material, then washed with water, dried, and evaporated. The residue, obtained in quantitative yield, crystallised from chloroform–ether in canary-yellow needles, m. p. 229° (decomp.); the colour was not removed by chromatographic adsorption from a chloroform solution and treatment with norit. The *compound* was sparingly soluble in organic solvents except chloroform and gave no colour with ferric chloride (Found: C, 55·8; H, 5·6. $C_{29}H_{36}O_5Br_2$ requires C, 55·8; H, 5·8%). When it was boiled with *o*-phenylenediamine in alcohol–acetic acid for 7 hours, it gave a colourlesss condensation product forming needles from alcohol, m. p. 248—249°.

Diketone (VII).—The oxidation of the pure β-ester with copper bronze was carried out as before. The crude product from 3 g. of ester was dissolved in benzene, ether added, and the pseudo-acidic material extracted with ice-cold 15% potassium hydroxide solution, a yellow potassio-derivative being precipitated. This was washed by decantation with ether, and the *diketone* liberated with mineral acid and extracted with ether, being obtained as a gum (2 g.) on evaporation of the solvent. It was finally purified by chromatographic adsorption from a benzene solution and thus freed from a small amount of adhering neutral impurity. It was eluted with benzene–methyl alcohol and finally with acetone, the progress of the operation being followed by the reaction with ferric chloride. The diketone was finally distilled at 130—140°/0·00064 mm. as a yellow gum (800 mg.) (Found : C, 77·7, 77·5; H, 9·1, 9·1. $C_{30}H_{42}O_4$ requires C, 77·3; H, 9·1%). The diketone readily formed an enol acetate on treatment with acetic anhydride and pyridine in the cold, but the compound was amorphous; it did not give a colour with ferric chloride.

Oxidation of the Diketone (VII).—This was carried out essentially as described on p. 718. The principal product was neutral; as it could not be induced to crystallise, the 2 : 4-*dinitrophenylhydrazone* was prepared. It was a scarlet powder, which was purified by chromatographic adsorption and crystallisation from acetic acid and then from alcohol; m. p. 274—276° (decomp.) (Found : C, 66·3; H, 6·9. $C_{31}H_{42}O_6N_4$ requires C, 65·7; H, 7·5%). $C_{31}H_{40}O_6N_4$ requires C, 65·9; H, 7·2%).

Reduction of the Diketone (VII).—1 G. of the diketone, purified through its potassio-derivative, was dissolved in 70 c.c. of alcohol and shaken with 50 mg. of Adams's catalyst in an atmosphere of hydrogen for 16 hours, 132 c.c. being absorbed at N.T.P. (theoretical for 3 mols., 146 c.c.). The pale yellow gum recovered on evaporation of the solvent was dissolved in benzene and percolated through a column of 20 g. of activated alumina, most of the material remaining adsorbed, although a small portion was recovered from the solution and solidified on rubbing with methyl alcohol. The material was then eluted from the column by means of benzene containing 1% of ethyl alcohol, the solution evaporated, and the residue dissolved in methyl alcohol and seeded with the crystalline material; after keeping in a refrigerator for 30 hours the crystals (150 mg.) were collected and recrystallised twice more, forming needles, m. p. 218—219°; the *tetrahydro*-compound gave no colour with ferric chloride (Found : C, 76·8; H, 10·1. $C_{30}H_{46}O_4$ requires C, 76·6; H, 9·9%). Owing to the small amount of material available the light absorption could only be measured approximately; a 0·0054% alcoholic solution showed a band head between 2740 and 2840 A. ($E^{1\%}_{1\,cm.}$ *ca.* 0·4). The 2 : 4-dinitrophenylhydrazone was an orange powder, m. p. 234—236°.

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