850. *The Structure of Bassic Acid.*[1]

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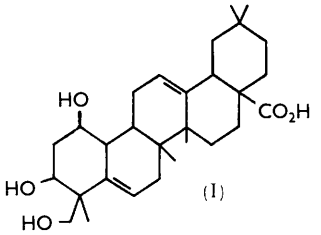
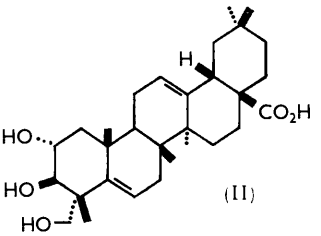
The conversion of bassic acid and of anhydroterminolic acid into a common derivative by periodate oxidation established the structure of the former as 2,3,23-trihydroxyolea-5,12-dien-28-oic acid. Methyl 23-deoxybassate readily formed an isopropylidene derivative, showing that the 2- and the 3-hydroxyl group are in *cis*-relation. Borohydride reduction of a derived *vic*-diketone, regenerating methyl deoxybassate, established the complete formula of bassic acid as 2β,3β,23-trihydroxyolea-5,12-dien-28-oic acid.

BASSIC acid is widely distributed as glycosides in the saponins of many plants of the order *Sapotacea*[2] and was first isolated in a pure form and investigated in detail by Heywood, Kon, and Ware,[3] who classed it as a trihydroxydienoic acid of the triterpene series and assigned to it the structure (I). This work has recently been summarised[4] and it has been pointed out that the experimental results on which this structure was based could be re-interpreted and did not exclude a 2,3,23(or 24)-trihydroxy-structure. It was further pointed out that no conclusive reasons for allocating an oleanane skeleton to bassic acid had been put forward. We also had been unconvinced of the validity of Kon's arguments since we became interested in bassic acid after its isolation from *Mimusops heckelii* (Makoré) in this laboratory,[5] and we have reinvestigated the chemistry of the acid.



(I)



(II)

From the beginning our efforts were turned towards the conversion of bassic acid and anhydroterminolic acid[6] (II) into a common derivative. The latter is isomeric with bassic acid and has both double bonds in the same position as suggested for the double bonds of that acid.

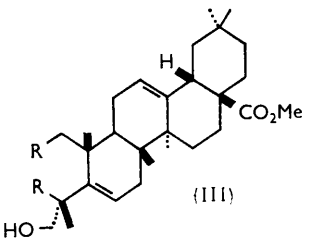
No difficulty was found in obtaining bassic acid from commercially available Mowrah meal. The best results came from the use of meal with a low fat content (*ca.* 1—2%), when a preliminary extraction with light petroleum was unnecessary. Percolation of such meal at 40° with 80% ethanol gave an extract which was readily hydrolysed by acid, the bassic acid produced being most easily purified through the sodium salt. In this way yields of about 0·5% of the meal may be obtained.

Much of our earlier work was based on the erroneous assumption that bassic acid did not react with periodate and thus lacked a *vic*-glycol function. Such a result was reported by the earlier workers and was, early in our own work, confirmed independently by both the present authors. However, our inability to reconcile many of our experimental findings with the 1,3-arrangement of the secondary hydroxyl groups in bassic acid led us to repeat the periodate oxidation which was then successful. We are unable to explain the earlier failures.

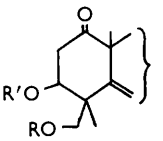
[1] For a preliminary communication see King and Yardley, *Proc. Chem. Soc.*, 1959, 393.
[2] Heywood and Kon, *J.*, 1940, 713.
[3] Heywood, Kon, and Ware, *J.*, 1939, 1124.
[4] Simonsen and Ross, " The Terpenes," Cambridge Univ. Press, 1957, Vol. V, pp. 139—147.
[5] King, Baker, and King, *J.*, 1955, 1338.
[6] King and King, *J.*, 1956, 4469.

The product of periodate fission of methyl bassate was crystalline and a similar degradation of methyl anhydroterminolate gave an identical product which must have structure (III; R = CHO). The identity was further confirmed by comparison of the triols (III; R = CH_2·OH) formed by borohydride reduction of both specimens of the dialdehyde. This result established the structure, including the stereochemistry, of bassic acid with the exception of the configuration of the secondary hydroxyl groups. The α-(hydroxymethyl)-carbonyl nature of the fission product was confirmed when alkali afforded formaldehyde. The dialdehyde which would be the other product of this reverse aldol reaction failed to crystallise and presumably had undergone further base-catalysed reactions.

The highly crystalline isopropylidene derivative of methyl bassate, and its oxidation to the corresponding dehydro-derivative, were described by the earlier workers [2,3] who assigned to it the partial structure (IV; R + R′ = $Me_2C<$). We repeated this preparation with the aim of removing the carbonyl-oxygen atom. The chromic oxide–sulphuric acid–acetone [7] reagent was found to be greatly superior in this preparation to other common oxidising agents, *e.g.*, chromic oxide in acetic acid or pyridine, or acetone–aluminium t-butoxide. The derived dihydroxy-compound was stable to alkali, a fact which we found incompatible with its formulation as (IV; R = R′ = H) which would be expected



(III)



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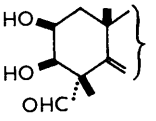

(V)

to be dehydrated under these conditions. Methyl dehydroisopropylidenebassate was readily converted into methyl deoxybassate by a modified Huang-Minlon reduction of its hydrazone followed by acid hydrolysis and re-esterification. Standard Huang-Minlon conditions resulted only in partial removal of oxygen and the vigorous conditions described by Barton, Ives, and Thomas [8] gave low yields. The realisation that methyl dehydrobassate is an aldehyde (partial structure V) initially followed from the failure of repeated attempts to isolate formaldehyde from pyrolysis of methyl deoxybassate with copper bronze. This reaction, in the triterpene series, is regarded as characteristic of a 1,3-secondary-primary glycol and is given by methyl bassate.[3] The result showed that the free hydroxyl group in methyl isopropylidenebassate must be part of the 1,3-glycol system and must almost certainly be the primary hydroxyl group. This conclusion was confirmed by a study of the nuclear magnetic resonance spectrum of methyl dehydroisopropylidenebassate and of its semicarbazone. The aldehyde shows a singlet peak with τ 1·04, a higher value than usual for an aldehyde (*ca.* 0·35) but not attributable to any other than an aldehydic proton. The high value has stereochemical implications because the τ values for the aldehyde protons of the fully substituted equatorial aldehyde vinhatical [8] and its axial epimer, vouacapenal,[9] are 0·77 and 0·23 respectively. The presence of a singlet (τ 3·01) in the spectrum of the semicarbazone confirmed the above conclusions.[10]

In the light of present knowledge these results mean that the isopropylidene group in methyl isopropylidenebassate must bridge the 2,3-positions, and thus methyl deoxybassate must be a *vic*-glycol. Its fission by periodate confirmed this conclusion. Of the four possible arrangements of the hydroxy-groups only two would easily give an isopropylidene

[7] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.
[8] Barton, Ives, and Thomas, *J.*, 1955, 2056.
[9] Godson, King, and King, *J.*, 1955, 1117.
[10] Curtin, Gourse, Richardson, and Rinehart, jun., *J. Org. Chem.*, 1959, **24**, 93.

derivative, namely, the *cis*-αα- and the *cis*-ββ-glycols.[11] It has been pointed [12] out that no 2α,3α-glycol of the steroid or triterpene field occurs in Nature, so the presumption would be that bassic acid has the 2β,3β-configuration. Confirmation of this was sought by borohydride reduction of a derived 2,3-diketone, borohydride reduction of both 2- and 3-ketones in steroids and triterpenes being known to produce predominantly β-alcohols.[13] Methyl deoxybassate itself failed to afford a pure product on oxidation, but the bromo-lactone obtained from deoxybassic acid was oxidised readily by chromic oxide in acetic acid to a yellow crystalline compound having the spectral characteristics of a non-enolised *vic*-diketone and affording a quinoxaline with *o*-phenylenediamine. The un-enolised nature of this diketone is in marked contrast with that of the 4-demethyl-2,3-dione derivable [14] from hederagenin, and also with those members of the cucurbitacin group having the appropriate oxidation state.[15]

Professor Ourisson of Strasbourg has interested himself in this anomaly and tells us that the un-enolised nature of the diketone is due to its preparation under acid conditions and to its very slow rate of enolisation in neutral solutions. After brief treatment with alkali the expected diosphenol structure can be demonstrated by the positive ferric reaction and by ultraviolet and infrared absorption.

Borohydride reduction of the yellow diketone readily regenerated deoxybassic bromo-lactone, characterised by its diacetate and by reduction and methylation to methyl deoxybassate.

Djerassi and his co-workers [12,16] have used the rate of cleavage by lead tetra-acetate to determine the stereochemistry of 2,3-diols of both steroidal sapogenins and triterpenes, *e.g.*, medicagenic acid (2β,3β-diol) and arjunolic and asiatic acid (2α,2β-diols). A good determination of the rate of cleavage of methyl bassate under the conditions used by these authors was not possible because of the rapidity of the reaction, which gave an approximate rate constant of 500×10^{-3} l. mole^{-1} sec.$^{-1}$. This is so much larger than that of any previously measured triterpene 2,3-glycol (medicagenic acid: $k = 31 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$) that it must be assumed that the presence of the 5,6-double bond has a marked accelerating affect on the fission, and it would clearly be unjustifiable to make stereochemical deductions from this result. It is relevant that the Δ^5-derivative (yuccagenin) of gitogenin is oxidised some 3·5 times faster than gitogenin itself.

Kon and his co-workers [2,3] reported the existence of two forms of methyl bassate, one obtained by esterification with diazomethane or dimethyl sulphate and alkali (the α-form), the other obtained by the use of methyl iodide and alkali [17] (the β-form). These were reported as forming different acetates but the same isopropylidene derivative, and to differ markedly in their response to catalytic hydrogenation. We have been unable to substantiate this claim and in all cases our methyl bassate has corresponded in its properties and those of its derivatives with those recorded for β-methyl bassate.

New derivatives of bassic acid that we have made during this investigation include methyl 11,13(18)-dehydrobassate, obtained by the action of selenium dioxide on methyl triacetylbassate and subsequent hydrolysis. The optical properties of this conjugated diene are characteristic, and its formation is further evidence for the derivation of bassic acid from oleanolic acid.[18] The ready formation of the bromo-lactone of both bassic and deoxybassic acid was also an early confirmation of the basic skeleton. Further, we were able to oxidise diacetyldeoxybassic bromo-lactone to a crystalline 1,2-epoxide (presumably

[11] Slates and Wendler, *Chem. and Ind.*, 1955, 167.
[12] Djerassi, Thomas, Livingston, and Thompson, *J. Amer. Chem. Soc.*, 1957, **79**, 5292.
[13] See, for instance, King, King, and White, *J.*, 1958, 2830; Dauben, Glanz, jun., Jiu, and Micheli, *J. Amer. Chem. Soc.*, 1956, **78**, 3752.
[14] Ruzicka, Jeger, and Norymberski, *Helv. Chim. Acta*, 1944, **27**, 1185.
[15] See, for instance, Enslin, Hugo, Norton, and Rivett, *J.*, 1960, 4779; Lavie and Shvo, *Chem. and Ind.*, 1959, 429.
[16] Djerassi and Ehrlich, *J. Org. Chem.*, 1954, **19**, 1351.
[17] van der Haar, *Rec. Trav. chim.*, 1929, **48**, 1155, 1166.
[18] Ruzicka and Jeger, *Helv. Chim. Acta*, 1942, **25**, 775; Barton and Holness, *J.*, 1952, 78.

the 5,6α-epoxide), thus affording the only conclusive chemical evidence for the existence of the second double bond in bassic acid. In a similar way to the corresponding derivative of anhydroterminolic lactone, epoxybassic bromo-lactone with hydrogen chloride gave a chlorohydrin which was inert to oxidation with chromic oxide and reconverted into the epoxide in warm pyridine.

Olea-5,12-diene-2,3,23,28-tetraol and -2,3,28-triol have also been prepared by reduction of, respectively, methyl bassate and methyl deoxybassate with lithium aluminium hydride.

Experimental

Nuclear magnetic resonance data were obtained with a Varian Associates instrument operating at 40 Mc./sec. in deuterochloroform. Optical rotations were measured, except where indicated, in chloroform solution at 20° and for the D-line.

Extraction of Mowrah Meal.—Mowrah meal (51 kg.; fat content 1·6%) was stirred with ethanol (80 l.) at 40° for 8 hr. The extract was recovered by decantation and the procedure was repeated with a further 80 l. of solvent. The combined extracts were concentrated to 8 l. and added with stirring to ether (20 l.). The saponin (" Mowrin ") which separated as a viscous golden-brown gum was immediately dissolved in 60% ethanol (30 l.) and the solution, in 2·5 l. portions, was boiled for 6—8 hr. with a 1 : 1 mixture (120 c.c.) of concentrated hydrochloric and sulphuric acid. Bassic acid separated from the hot solution as a coarse sand-coloured powder (30—50 g.) which was washed repeatedly with boiling 80% aqueous ethanol. A cold suspension of the impure acid (30—50 g.) in cold 60% aqueous ethanol (*ca.* 1 l.) was made weakly alkaline (pH 9—10) with concentrated aqueous sodium hydroxide, and the filtered dark solution was treated with an excess of sodium hydroxide (30—40 g.) and, after addition of charcoal, was again filtered. It was then evaporated on a steam-bath until a test portion crystallised on cooling. The sodium bassate so obtained separated from aqueous methanol as colourless rods (yield 20—30 g.). The total yield from the extraction was 280 g.

The acid separated from an acidified solution of the sodium salt in gelatinous form and for further experiments the salt was converted directly, in 75% yield, into the methyl ester by reaction in aqueous methanol with dimethyl sulphate and 10% aqueous sodium hydroxide. The ester separated from aqueous methanol as the *hemihydrate*, m. p. 180—190°, [α] +58° (*c* 0·52) (Found: C, 73·0; H, 9·5. $C_{31}H_{48}O_5,\frac{1}{2}H_2O$ requires C, 73·0; H, 9·7%). The anhydrous ester was obtained by crystallisation from acetone and had m. p. 216—218° after sintering at 192° (Found: C, 74·2; H, 9·5. Calc. for $C_{31}H_{48}O_5$: C, 74·4; H, 9·7%). Heywood and Kon [1] give for β-methyl bassate, m. p. 216—217°, [α] +56°. The identity of our material with bassic acid was checked by the preparation of the following derivatives (published constants in parentheses): bromo-lactone,[2] m. p. 220° (220°); isopropylidene-bromo-lactone,[2] m. p. 205—207° (205—206°); methyl triacetylbassate,[2] m. p. 149—150° (148—149°); methyl isopropylidenebassate,[3] m. p. 206—208° (205—206°).

Oxidation of Methyl Bassate and Methyl Anhydroterminolate with Periodate.—(*a*) Methyl bassate (250 mg.) in ethanol was treated with aqueous *ca.* 0·25M-sodium metaperiodate (10 c.c.), and the volume adjusted to 100 c.c. with ethanol. The mixture was kept at room temperature in the dark and the excess of periodate was estimated in the usual way (in 20 c.c. portions) at various times. Appropriate blank determinations were made at each time and the following results, expressed as percentage oxidation of one *vic*-glycol unit, were obtained; 3 hr. 53%; 8 hr. 70%; 23 hr. 95%. (*b*) An alcoholic solution of methyl bassate (1 g. in 200 c.c.) mixed with aqueous sodium metaperiodate (1 g. in 20 c.c.) was set aside at room temperature in the dark for 48 hr. The mixture was poured into water. The precipitated *dialdehyde* (III; R = CHO) crystallised from aqueous methanol (charcoal) in prisms (630 mg.), m. p. 183° (decomp.), [α] +183° (*c* 0·78) (Found: C, 73·5; H, 8·95. $C_{31}H_{46}O_5,\frac{1}{2}H_2O$ requires C, 73·3; H, 9·3%).

Oxidation of methyl anhydroterminolate (1 g.) in the same way (*b*) gave a product (470 mg.), m. p. 183° (decomp.) undepressed by the product from methyl bassate, [α] +188° (*c* 0·53) (Found: C, 73·6; H, 9·1%). The infrared absorption of the two specimens was identical.

Both specimens of the aldehyde were reduced in pyridine–methanol with an excess of potassium borohydride and gave the *triol* (III; R = CH_2·OH), rods (from methanol), m. p. 216°, [α] +88° (*c* 1·21) (Found: C, 74·0; H, 9·8. $C_{31}H_{50}O_5$ requires C, 74·1; H, 10·0%).

Alkaline Decomposition of the Dialdehyde.—The dialdehyde (200 mg.) in 3 : 7 v/v aqueous methanol (100 c.c.) containing potassium hydroxide (4 g.) was set aside overnight at room

temperature. The solution was made acid to Congo Red and distilled. Dimedone (70 mg.) was added to the distillate and after 30 min. the solution was concentrated to 20 c.c.; needles of the formaldehyde–dimedone compound (7·4 mg.) separated. It was identified by m. p. and mixed m. p. No crystalline compound could be isolated corresponding to the major fragment of the molecule.

Methyl Dehydroisopropylidenebassate.—A stirred suspension of methyl isopropylidenebassate (6·8 g.) in pure acetone (300 c.c.) was treated dropwise at 0—5° during 1 hr. with 6·3 c.c. of a solution prepared from chromic oxide (3 g.) concentrated sulphuric acid (2·8 c.c.) and water (15 c.c.). After a further 30 min. the mixture was diluted to 1 l., and the product was washed with potassium carbonate solution and water and purified by passage of its solution in benzene down a short column of alumina. After removal of benzene and crystallisation of the residue from methanol, methyl dehydroisopropylidenebassate (5·2 g.) separated in prisms m. p. 181—183° (lit.,[2] m. p. 181—183°) (Found: C, 76·0; H, 9·2. Calc. for $C_{34}H_{50}O_5$: C, 75·8; H, 9·4%). The *hydrazone*, prepared in boiling ethanol, crystallised from methanol as rods, m. p. 184—186°, [α] +39° (*c* 0·96) (Found: C, 73·9; H, 9·5; N, 5·1. $C_{34}H_{52}N_2O_4$ requires C, 73·7; H, 9·4; N, 4·9%); the *semicarbazone hydrate* formed rods (from aqueous ethanol), m. p. 171—174°, [α] +23·5° (*c* 0·85) (Found: C, 68·7; H, 9·1; N, 6·7. $C_{35}H_{53}N_3O_5,H_2O$ requires C, 68·5; H, 9·0; N, 6·85%).

Methyl Dehydrobassate.—Hydrolysis of the above isopropylidene derivative in methanol containing a little hydrochloric acid gave the aldehyde as needles (from methanol), m. p. 201—202° (lit.,[2] m. p. 202—203·5°), unaffected by treatment with 5% ethanolic sodium hydroxide at room temperature overnight or at the b. p. for 1 hr. The *oxime* crystallised from methanol in needles, m. p. 220°, [α] +61° (*c* 0·44) (Found: C, 72·2; H, 9·4; N, 2·7. $C_{31}H_{47}NO_5$ requires C, 72·5; H, 9·2; N, 2·7%), and the *oxime diacetate* (prepared by use of acetic anhydride–pyridine) was prisms (from aqueous methanol), m. p. 140° (effervescence), [α] +64° (*c* 0·79) (Found: C, 70·4; H, 8·4; N, 2·2; Ac, 13·6. $C_{35}H_{51}NO_7$ requires C, 70·3; H, 8·6; N, 2·3; 2Ac, 14·6%).

Deoxybassic Acid.—A solution of sodium hydroxide (90 g.) and 100% hydrazine hydrate (40 c.c.) in ethylene glycol (1 l.) was distilled until it refluxed freely at 185°. Methyl dehydroisopropylidenebassate hydrazone (12 g.) was then added and the solution was boiled for 14 hr. and diluted with water. The crystalline precipitate in ethanol (250 c.c.) was treated at the b. p. with concentrated hydrochloric acid (2 c.c.) for 15 min., nearly pure *deoxybassic acid* (8·6 g.) rapidly separating. The very sparingly soluble acid was recrystallised for analysis from ethanol; it had m. p. 306—309° (decomp.), [α] +80° (*c* 1·09 in pyridine) (Found: C, 76·9; H, 9·9. $C_{30}H_{46}O_4$ requires C, 76·55; H, 9·85%). The *methyl ester* (prepared by use of diazomethane) crystallised from methanol in needles, m. p. 216—218°, [α] +69° (*c* 1·04) (Found: C, 76·9; H, 9·65; OMe, 7·3. $C_{31}H_{48}O_4$ requires C, 76·8; H, 10·0; 1OMe, 6·4%). *Methyl deoxyisopropylidenebassate*, prepared in acetone containing a trace of hydrochloric acid, crystallised from acetone in thin prisms, m. p. 157—159°, [α] +51° (*c* 0·79) (Found: C, 77·6; H, 9·6. $C_{34}H_{52}O_4$ requires C, 77·8; H, 10·0%). The *methyl ester diacetate* (obtained by using acetic anhydride–pyridine) formed flat prisms, m. p. 109—111°, [α] +44·5° (*c* 0·99), from aqueous methanol (Found: C, 73·9; H, 9·1; Ac, 16·9. $C_{35}H_{52}O_6$ requires C, 73·9; H, 9·2; 2Ac, 15·2%). Under the conditions previously used the methyl ester consumed periodate corresponding to the presence of 91·5% of one *vic*-glycol unit in 42 hr.

Methyl deoxybassate failed to give formaldehyde when heated with activated copper bronze at 270—290° or in refluxing biphenyl. That methyl bassate afforded formaldehyde under these conditions [3] was confirmed.

Deoxybassic Bromo-lactone.—Bromine (1·6 g.) in acetic acid (25 c.c.) was added during 30 min. to a heated (100°) and stirred suspension of finely powdered deoxybassic acid (4 g.) in acetic acid (250 c.c.) containing sodium acetate (16 g.). After a further 10 min. nearly all the acid dissolved and the solution was filtered and poured into water containing a little sodium hydrogen sulphite. The precipitate crystallised from methanol (charcoal) to give the *bromolactone* as colourless needles, m. p. 236—250° (decomp.), [α] +77° (*c* 1·03) (Found: C, 65·7; H, 8·5; Br, 13·0. $C_{30}H_{45}BrO_4$ requires C, 65·6; H, 8·25; Br, 14·5%); light absorption (in ethanol) ε_{210} 1600; ε_{220} 370; $\nu_{max.}$ (in CCl_4) 1770 cm.$^{-1}$. The bromo-lactone was reconverted into deoxybassic acid by zinc dust in acetic acid at 100° for 2 hr. The *diacetate* (acetic anhydride–pyridine) formed plates (from aqueous methanol), m. p. 231—232° [α] +74° (*c* 0·65) (Found: C, 64·5; H, 8·0; Br, 11·2; Ac, 15·7. $C_{34}H_{49}BrO_6$ requires C, 64·4; H, 7·8; Br, 12·6; 2Ac, 13·6%). The

isopropylidene derivative did not separate when prepared in acetone–hydrochloric acid, but was precipitated when its solution was poured into dilute ammonia. From methanol or aqueous methanol it formed rods, m. p. 214°, [α] +48° (*c* 0·43) (Found: C, 67·4; H, 8·4; Br, 12·9. $C_{33}H_{49}BrO_4$ requires C, 67·2; H, 8·4; Br, 13·5%).

Oxidation of Deoxybassic Bromo-lactone.—To a stirred and cooled suspension of deoxybassic bromo-lactone (2·3 g.) in acetic acid–water–sulphuric acid (250 c.c.; 50 c.c.; 0·25 c.c. of concentrated acid) was added, during 1 hr., a solution of chromic oxide (1 g.) in acetic acid (35 c.c.). After a further 10 min. the excess of reagent was reduced with sodium hydrogen sulphite and the solution was poured into water. The precipitate crystallised from ethanol–chloroform, to give the *diketone* as small yellow prisms (1 g.), m. p. 224° (decomp.), [α] +80° (*c* 0·4) (Found: C, 65·5, 65·7; H, 7·9, 7·2. $C_{30}H_{41}BrO_4$ requires C, 66·0; H, 7·6%), $\lambda_{max.}$ (in $CHCl_3$) 274 (ε 420) and 420 (ε 22) mμ. The colour was not removed by charcoal or by chromatography on alumina, and the compound gave no colour with ferric chloride. It formed a *mono-2,4-dinitrophenylhydrazone*, pale yellow needles, m. p. 264° (decomp.) (Found: C, 59·7; H, 6·4; Br, 10·9; N, 7·5. $C_{36}H_{45}BrN_4O_7$ requires C, 59·6; H, 6·25; Br, 11·0; N, 7·7%), $\lambda_{max.}$ (in $CHCl_3$) 249 (ε 10,000) and 372 (ε 26,300) mμ. The *quinoxaline derivative* prepared with *o*-phenylenediamine in acetic acid crystallised from methanol–chloroform in buff-coloured rods, m. p. 238° (decomp.) (Found: C, 70·3; H, 7·5; N, 4·5. $C_{36}H_{45}BrN_2O_2$ requires C, 70·0; H, 7·65; N, 4·5%), $\lambda_{max.}$ (in $CHCl_3$) 239 (ε 31,700), 310 (inflexion, ε 7800), and 321 (ε 9900) mμ. Leonard and Mader [19] give for the quinoxaline from 3,3,6,6-tetramethylcyclohexane-1,2-dione $\lambda_{max.}$ 238 (ε 31,000), 310 (ε 7900), and 321 (ε 9800) mμ.

A pyridine–methanol solution of the diketone (300 mg.) with an excess of potassium borohydride overnight afforded 170 mg. of pure deoxybassic bromo-lactone. The identity of the product was confirmed by the preparation of the acetate and by reduction to deoxybassic acid characterised as its methyl ester. In each case identity was established by mixed m. p. and identity of infrared absorption.

Methyl 11,13(18)-*Dehydrobassate.*—Methyl triacetylbassate (300 mg.) was heated with selenium dioxide (300 mg.) in boiling acetic acid (30 c.c.) for 3 hr. The product precipitated with water was hydrolysed for ½ hr. with boiling 5% methanolic potassium hydroxide, and then water precipitated the *triene* (160 mg.) which crystallised from methanol in rods, m. p. 240—244°, [α] −195° (*c* 0·33) (Found: C, 74·4; H, 8·9. $C_{31}H_{46}O_5$ requires C, 74·7; H, 9·3%), $\lambda_{max.}$ (in EtOH) 243 (ε 24,650), 250 (ε 27,150), and 258 (ε 16,700) mμ.

Diacetylepoxydeoxybassic Bromo-lactone.—Diacetyldeoxybassic bromo-lactone (1 g.) in acetic acid (15 c.c.) was treated at 100° for 3 hr. with an excess of 30% hydrogen peroxide (0·7 c.c.). The *product* was isolated by dilution, and crystallised from methanol as plates (600 mg.), m. p. 230°, [α] +56° (*c* 0·71) (Found: C, 62·6; H, 7·4; Br, 11·9. $C_{34}H_{49}BrO_7$ requires C, 62·85; H, 7·6; Br, 12·5%).

2,3-*Diacetyl*-6-*chloro*-5-*hydroxydeoxybassic Bromo-lactone.*—The above epoxide (0·5 g.) was treated in chloroform with hydrogen chloride at room temperature for 1 hr. After removal of the solvent the residue crystallised from aqueous acetone, giving the chlorohydrin (0·27 g.) as thin rods, m. p. 238° (decomp.) (Found: C, 59·4; H, 7·3. $C_{34}H_{50}BrClO_7$ requires C, 59·5; H, 7·35%). The chlorohydrin reverted to the epoxide in warm pyridine and was recovered after treatment with an excess of chromic oxide in acetic acid–sulphuric acid at room temperature for 5 days.

Olea-5,12-*diene*-2,3,23,28-*tetraol.*—Methyl bassate (1 g.) was reduced in tetrahydrofuran (40 c.c.) with an excess of lithium aluminium hydride at the b. p. for 3 hr. Working up in the usual way gave the *tetra-ol* as prisms m. p. 216—219°, [α] +56° (*c* 0·33), from aqueous methanol or ethyl acetate (Found: C, 76·0; H, 10·0. $C_{30}H_{48}O_4$ requires C, 76·2; H, 10·2%).

Olea-5,12-*diene*-2,3,28-*triol.*—Methyl deoxybassate was reduced as in the previous experiment and gave the *triol* which crystallised from benzene as dense prisms, m. p. 179—181°, [α] +63° (*c* 0·68) (Found: C, 78·7; H, 10·1. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·3%).

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