382. *Experiments on the Constitution of the Aloins. Part III.*

By R. S. CAHN and J. L. SIMONSEN.

WHILST accepting Léger's empirical formula, $C_{20}H_{18}O_9$, for barbaloin (*inter alia*, *Ann. Chim.*, 1916, **6**, 318; 1917, **8**, 265), Gibson and Simonsen (J., 1930, 553) concluded that the product obtained therefrom by means of bromine-water was the trihalogeno-compound, $C_{16}H_{15}O_7Br_3$, the corresponding chloro-derivative being $C_{16}H_{15}O_7Cl_3$. Without advancing any new experimental evidence or offering an adequate explanation of the analytical discrepancies, Léger recently (*Bull. Soc. chim.*, 1931, **49**, 70) criticised this conclusion on the ground that these substances are oxidised by sodium peroxide to *tetra*bromo- and *tetra*chloro-aloe-emodin. This objection has been apparently strengthened by our observation that tribromopenta-acetylnorbarbaloin * is oxidised by chromic acid to tetrabromotriacetylaloe-emodin. In all these cases, however, the yield is very poor (cf. p. 2582), and in view of the well-known mobility of halogens we do not consider that the formation of the tetrahalogenated aloe-emodins can be considered to be a valid objection to the composition assigned to the parent halogen derivatives, the more so since we have been able to confirm conclusively the formula assigned to tribromonorbarbaloin. When tribromonorbarbaloin pentamethyl ether is treated with piperidine under the conditions described on p. 2582, it is partially demethylated (cf. Cahn, J., 1931, 1121), yielding a *trimethyl* ether, which, unlike the pentamethyl ether, is crystalline. Analyses of this substance agree only with the formula $C_{16}H_{12}O_4Br_3(OMe)_3$, and there can, therefore, no longer be any doubt that tribromonorbarbaloin must be $C_{16}H_{15}O_7Br_3$; by analogy, the chloro-derivative is $C_{16}H_{15}O_7Cl_3$.

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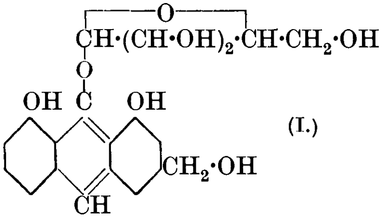
* In the light of the formulæ developed in this paper, the correct name for this substance is tribromopenta-acetylbarbaloin, but to prevent confusion the name used in the previous communication is used here also.

The successful methylation of the bromo-derivatives led us to attempt once more that of barbaloin itself, in spite of the failures previously reported (Jowett and Potter, J., 1905, **87**, 878; Robinson and Simonsen, J., 1909, **95**, 1085). We now find that repeated treatment with Purdie's reagent gives an excellent yield of a colourless, crystalline substance, m. p. 177—179°, which is either a *pentamethyl* or a *heptamethyl* ether, $C_{16}H_{13}O_2(OMe)_5$ or $C_{20}H_{15}O_2(OMe)_7$.

Whilst these experiments were in progress, Hauser (*Pharm. Acta Helv.*, 1931, **6**, 79) reported the fundamental observation that digestion of barbaloin with borax solution gives aloe-emodin-anthranol, $C_{15}H_9O(OH)_3$. Rosenthaler (*ibid.*, 1930, **5**, 59; 1931, **6**, 115; 1932, **7**, 19; *Arch. Pharm.*, 1932, **270**, 214) considers this reaction to be a simple hydrolysis of barbaloin to arabinose and the anthranol; he thus assigns formula (I) to barbaloin, which he considers to be $C_{20}H_{20}O_8$. He suggests that barbaloin crystallises



(I.)

with $1{\cdot}5H_2O$, although his own analyses do not conclusively support this view, and he offers no explanation of the disagreement with the many previously reported analyses of barbaloin and its derivatives which adoption of this new formula would entail. We have confirmed the production of the anthranol; its formula has been confirmed by analysis and by reduction to the *dihydro*-derivative, $C_{15}H_{14}O_4$. We also find, however, that the borax fission yields methyl alcohol; arabinose is not formed, nor is formaldehyde or formic acid.

The three sets of observations recorded above led us to make a comprehensive survey of the evidence upon which the formula of barbaloin is based. It would appear at first sight that molecular-weight determinations should determine whether the formula of barbaloin has 16 or 20 carbon atoms. However, the results obtained by different investigators are contradictory, and for some reason, still to be explained, barbaloin and its derivatives behave abnormally in solution. Thus Jowett and Potter (*loc. cit.*) and Aschan (*Arch. Pharm.*, 1903, **241**, 346) record values in agreement with the formula $C_{16}H_{18}O_7$ (*M*, 322). Dr. Soper has carried out in these laboratories a series of very careful cryoscopic determinations, using a sealed apparatus which precluded all possibility of vitiation of the results by atmospheric moisture; he found the molecular weight of carefully dehydrated barbaloin to be 361·4 in acetic acid and 269·0 in phenol. By the ebullioscopic method, Seel and Kleber (*Ber.*, 1916, **49**, 2364) obtained values in agreement with a C_{20} formula when acetone was used as solvent, but record the remarkable observation that no elevation of the boiling point occurs at all when acetic acid or ethyl acetate is used. The halogen derivatives give equally contradictory results. The formula, $C_{16}H_{15}O_7Br_3$, for tribromonorbarbaloin is confirmed by cryoscopic determinations in phenol (Jowett and Potter) and by ebullioscopic determinations in acetone (Sugden). On the other hand, Professor Sugden obtained results for the penta-acetyl derivatives of tribromo- and trichloronorbarbaloin agreeing with the C_{20} formula. The methyl ether has been found by Professor Sugden by the ebullioscopic method, using acetone, and by Dr. Soper by the cryoscopic method, using acetic acid, to have a molecular weight of about 500, which would derive it from the C_{20} formula. The association of methyl ethers is unusual, but it is noteworthy that it has been recently observed for octamethylcellobiose and endecamethylcellotriose (Ullmann and Hess, *Naturwiss.*, 1932, **20**, 316). Although it is permissible to explain the high molecular weights by association, we consider that it would be dangerous to base any conclusions on these results and prefer, therefore, to consider only the direct chemical evidence.

It is convenient to examine first the evidence which may be regarded as supporting the C_{20} formula, *viz.*: (i) the oxidation of the trihalogeno-norbarbaloins to tetrahalogenoaloe-emodins; (ii) the formation of tribromobarbaloin, m. p. 291°, by bromination in hydrobromic acid solution; (iii) the conversion of barbaloin into aloe-emodin and arabinose by acids; and (iv) the formation of aloe-emodinanthranol by the action of borax.

The first of these points has been dealt with already and is referred to again below. Analyses of tribromobarbaloin, m. p. 291°, undoubtedly agree with a C_{20} formula, if the simple molecular weight be assumed, and this evidence led Gibson and Simonsen (*loc. cit.*) to retain Léger's formula. This substance, however, differs completely in properties from all other aloin derivatives, and Léger is quite possibly correct in suggesting that it is a condensation product, perhaps of dianthraquinonyl type, rather than a true derivative of barbaloin. It has resisted our repeated attempts at degradation, and we can, as yet, offer no suggestion as to its true nature.

The conversion of pure barbaloin into arabinose and aloe-emodin, the fundamental basis of Léger's formula, occurs in such poor yield and only under such abnormal conditions (*viz.*, boiling for one hour and keeping for several months) that in our opinion it cannot be a *simple* hydrolysis either of a glycoside or of an ether. The formation of arabinose in this reaction and of aloe-emodin and its derivatives in this and other degradative reactions indicates the presence of potential anthraquinone and pentose units in the barbaloin molecule, but it does not of necessity imply that they are present as such, as has been assumed by the advocates of the C_{20} formulæ. Our failure to isolate arabinose from the products of the borax fission appears to us to destroy the value of this reaction as an argument in favour of Léger's formula.

On the other hand, the evidence against a C_{20} formula is overwhelming, and we revert now to the formula $C_{16}H_{18}O_7$, originally proposed by Tilden (J., 1872, **25**, 204; 1875, **28**, 1275; 1877, **32**, 267). First, barbaloin methyl ether is colourless, whereas it would be expected to be yellow on Léger's or Rosenthaler's formula. Secondly, the halogenonorbarbaloins are derived from a parent substance, $C_{16}H_{13}O_2(OH)_5$, whilst aloe-emodinanthranol is $C_{15}H_9O(OH)_3$. The conversion of $C_{20}H_{12}O_3(OH)_6$ (Léger) or $C_{20}H_{14}O_2(OH)_6$ (Rosenthaler) into these substances involves loss in one case of C_4O_2 or C_4H_2O, one hydroxyl group disappearing, and in the other of $C_5H_6O_5$ or $C_5H_8O_4$, three hydroxyl groups disappearing. We are unable to see how any formula can be devised which will allow both changes to be represented intelligibly.

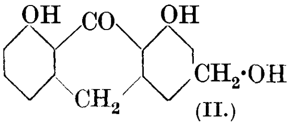
The analytical evidence is equally conclusive. The following results for our highly crystalline barbaloin methyl ether, which does not retain solvent, are characteristic :

		Calc. for					
		$C_{16}H_{13}O_2(OMe)_5$.	$C_{20}H_{12}O_3(OMe)_6$.	$C_{20}H_{11}O_3(OMe)_7$.	$C_{20}H_{14}O_2(OMe)_6$.	$C_{20}H_{13}O_2(OMe)_7$.	$C_{20}H_{15}O_2(OMe)_7$.
	Found.	Tilden.	Léger.		Rosenthaler.		
C	64·5, 64·7, 64·3	64·3	64·2	64·8	66·1	66·6	64·2
H	7·2, 7·1, 7·1	7·1	6·2	6·45	6·8	7·0	7·2
OMe ...	40·7	39·5	38·2	43·4	39·2	44·6	43·0

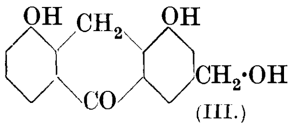
Rosenthaler's formula is definitely excluded, Léger's somewhat less definitely. We do not consider our three analyses are open to question, since they were made with three distinct specimens; the first two are micro-analyses by Dr. A. Schoeller, Berlin (to whom also the methoxyl determination is due), and Mr. Boston, Liverpool, and the third is a macro-analysis by one of the present authors. It is unnecessary to tabulate the analyses of barbaloin and its derivatives already recorded in the literature. Jowett and Potter's careful work strongly supports Tilden's formula, and examination of Léger's results reveals the remarkable fact that his analytical figures for barbaloin and the numerous derivatives prepared by him are on the average 1 unit % high in C and H for his formula, $C_{20}H_{18}O_9$, but agree perfectly (with one exception, a halogen derivative) for Tilden's formula, $C_{16}H_{18}O_7$.

So far as we have been able to discover, there is no chemical evidence directly contrary to the C_{16} formula, if we exclude the tetrahalogenated aloe-emodins, and we shall proceed now to discuss the structural formula to be assigned to barbaloin on this basis. It must satisfy the following requirements: (i) it must contain five hydroxyl groups and probably a carbonyl group, since barbaloin pentamethyl ether yields a red amorphous derivative with 2 : 4-dinitrophenylhydrazine; (ii) it must contain a phenolic hydroxyl group (aromatic ring), as barbaloin is soluble in alkali and gives a colour with ferric chloride; (iii) it must allow of the formation by mild hydrolysis of aloe-emodinanthranol and methyl alcohol; and (iv) it must permit fission to aloe-emodin and arabinose.

The simplest degradation product of barbaloin is undoubtedly the anthranol, the reaction being represented by the equation: $C_{16}H_{18}O_7 \longrightarrow C_{15}H_{12}O_4 + MeOH + H_2O + O$. The yield of anthranol is poor, but it can be increased appreciably, in agreement with this conception of the nature of the reaction, by addition of hydrazine as oxygen acceptor. In the absence of hydrazine there is probably a larger amount of intermolecular disproportionation, and these side reactions may account for the resinous by-products which are always formed along with the anthranol. It is of interest that Rosenthaler suggested the addition of phenylhydrazine, although he does not report any improvement in the yield. It is obvious that the anthranol may be represented by either (II) or (III), and in agreement with Rosenthaler (*loc. cit.*) we regard (II) as most probably correct, since the compound gives almost instantaneously a dark insoluble derivative with boroacetic



(II.)



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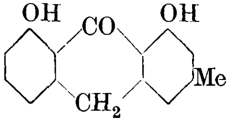
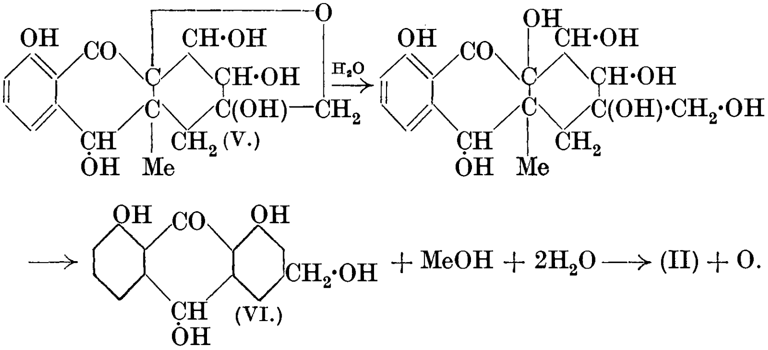


(IV.)

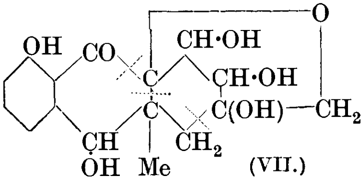
anhydride. Barbaloin itself gives a similar derivative, but very much more slowly, due, we believe, to the gradual formation of the anthranol. It is perhaps not without significance that Naylor and Garner (*J. Amer. Chem. Soc.*, 1931, **53**, 4114) have recorded the isolation of (IV) from commercial chrysarobin. On the basis of formula (II) for the anthranol, we suggest for barbaloin itself the representation (V), which comparatively readily explains all its reactions. The conversion into the anthranol might then proceed in accordance with the scheme :



We have, of course, no evidence of the order in which these changes occur, but we suggest that the addition of hydrazine is of value in increasing the yield by reducing the hydroxyanthrone (VI) at some stage in the reaction.

It will be agreed that this formula accounts readily for the formation of aloe-emodin and rhein by the action of oxidising agents, since elimination of the methyl group will in all cases cause the hydroaromatic ring to become aromatic by loss of water. It accounts also for the fact that barbaloin pentamethyl ether on oxidation with potassium permanganate yields rhein dimethyl ether and not aloemodin trimethyl ether, the formation of which would be anticipated if the $\cdot CH_2OH$ group had been methylated in the parent ether. Further, we have now found that ferric chloride readily oxidises barbaloin, giving aloe-emodin in a yield of 70%, so that this is now a comparatively readily accessible substance. This oxidation is likewise in accord with the suggested formula, since ferric chloride is one of the most useful reagents for the aromatisation of hydroaromatic rings.

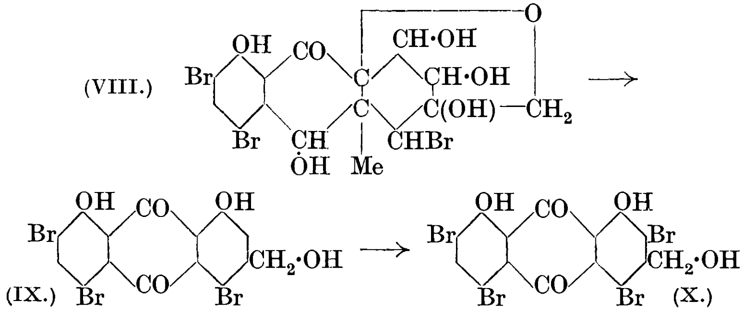
The suggested formula contains a preformed pyran ring, the degradation to arabinose involving the fission of C–C linkings as indicated by the dotted lines in (VII). We admit that we can point to no close analogy for a ring fission of this type, but the reaction leading to arabinose is so unusual and the yield so poor that we do not regard it as inherently impossible.



(VII.)

The distribution of the alcoholic hydroxyl groups in (V) is admittedly somewhat hypothetical. It is based essentially on the following considerations: (*a*) hydroxyl groups must be present in the 1 : 8-positions in which they appear in aloe-emodin; (*b*) the formula must include a potential pentose unit; (*c*) elimination of water from the right-hand ring must give a mono- and not a dihydroxylic aromatic ring; and (*d*) the hydroxyl group on the *meso*-carbon atom most readily accounts for the increased yield obtained when a reducing agent is added in the borax fission. A hydroaromatic ring of the type formulated would undoubtedly be extremely unstable and reactive, and it is probably the cause of the formation of the " aloin red " and the " aloin black," which have been so frequently described. The " aloin red " resembles in its general properties the phlobaphenes, which are probably in many cases catechol condensation products, and it is clear that catechol or a substituted catechol might under certain conditions be formed from barbaloin if the suggested formula be accepted.

We have no direct evidence enabling us to assign a formula to tribromonorbarbaloin, but we consider that it is most probably represented by (VIII). On oxidation this would undoubtedly partially undergo complete degradation, and the primary product of the oxidation, tribromoaloe-emodin (IX), would then be further brominated by the liberated bromine to yield the tetrabromoaloe-emodin (X). An attempt to convert tribromonorbarbaloin into



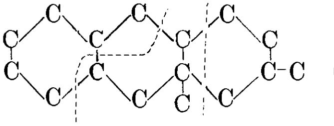
(VIII.)

(IX.)

(X.)

an anthranol by borax was unsuccessful, the bromide being recovered unchanged.

It will be seen that the formula now proposed for barbaloin can be constructed from one hexose and two isoprene units, as indicated by the dotted lines in the skeleton formula (XI). If further work


(XI.)

should substantiate the formula now assigned to barbaloin, the chemistry of synthetic purgatives will require reconsideration, and we venture to suggest that an essential feature of their structure will prove to be an oxide ring.

EXPERIMENTAL.

Barbaloin Pentamethyl Ether.—To a soln. of barbaloin (19 g.) in dry acetone (150 c.c.), MeI (200 g.) and Ag_2O (from 145 g. of $AgNO_3$) were gradually added, the mixture being heated on the water-bath for 10 hrs. The solvent was removed from the filtered solution and the resinous residue dried in vac. over H_2SO_4, redissolved in acetone, and treated with a further quantity of MeI (100 g.) and Ag_2O (from 70 g. of $AgNO_3$). The resin recovered from this methylation was now sol. in MeI and it was further methylated with the same quantity of reagents as used in the previous case, but the acetone being omitted. After completion of the reaction, acetone was added, the soln. filtered, the solvent and excess of MeI removed, and the residue dissolved in C_6H_6. Crystals (2 g.) were slowly deposited, and a further quantity was obtained when the filtrate was allowed to evaporate slowly in vac. Complete removal of the solvent gave a yellow gum, from which a further quantity of the Me ether was prepared by renewed methylation. *Barbaloin pentamethyl ether* (total yield, 13·8 g.) crystallises from abs. EtOH in highly iridescent, colourless, glistening prisms, m. p. 177—179° after sintering at 175° (analytical data on p. 2576); in $CHCl_3$ (c = 1·40) $[\alpha]_{5461}$ − 12·05°. In the earlier expts. it was found convenient to control the methylation by determination of the rotatory power, which gradually fell from $[\alpha]_{5461}$ − 32° after one treatment with MeI to − 12·5°. The ether is readily sol. in acetone, $CHCl_3$, AcOH, AcOEt, in hot C_6H_6, MeOH, and EtOH, but sparingly so in the last three solvents when cold; it is very sparingly sol. in H_2O, Et_2O, *cyclo*hexane, and ligroin. In EtOH it gives no colour with $FeCl_3$; it is stable to $KMnO_4$ in acetone and is not attacked by CrO_3 in hot AcOH. In $CHCl_3$ it readily absorbs Br with evolution of HBr, but the Br-derivative is a gum. When it was digested with $FeCl_3$ at 125—130° in aq. AcOH for 5 hrs., some resinification occurred, but the bulk of the ether was recovered unchanged. The ether reacted with 2 : 4-dinitrophenylhydrazine and with NH_2OH; the product with the former reagent was a bright scarlet powder, readily sol. in most org. solvents, whilst the latter gave a pale yellow gum, readily sol. in H_2O. It did not react with semicarbazide acetate. When it was heated with piperidine, resinification took place and a homogeneous product could not be isolated.

Oxidation of Barbaloin Pentamethyl Ether with Potassium Permanganate.—The ether (3·4 g.) was made into a paste with hot H_2O, and $KMnO_4$ aq. (2·5%; 365 c.c.) gradually added to the mixture which was warmed on the water-bath. The MnO_2 sludge was removed, and the bright yellow filtrate concentrated; the sparingly sol. K salt, which separated in soft yellow needles, was collected, redissolved in hot H_2O, and the soln. acidified. The yellow solid thus obtained (0·95 g.) crystallised from EtOH in yellow needles, m. p. 283—284°, and was identified as rhein dimethyl ether by a mixed m. p. determination and by esterification to methylrhein dimethyl ether, m. p. 183—185°, alone or in admixture with an authentic specimen. A further quantity of the ether (0·9 g.; total yield, 77%) was obtained from the original filtrate.

Aloe-emodinanthranol.—This was prepared by Hauser's method (*loc. cit.*) (yield, 1·1 g. from 10 g. of barbaloin), but a somewhat improved yield (1·8 g.) was obtained if N_2H_4 (1 g.) was added to the borax soln. prior to digestion. In two expts., steam was passed through the boiling soln. and the distillate tested for the presence of MeOH, which was detected by Denigès's method (*Compt. rend.*, 1910, **150**, 832, 529). Aloe-emodinanthranol crystallised from AcOH in yellow needles, m. p. 199° (Found: C, 70·3, 70·0; H, 4·8, 4·6. Calc. for $C_{15}H_{12}O_4$: C, 70·3; H, 4·7%). In EtOH the anthranol gives with $FeCl_3$ a reddish-brown colour, which disappears on warming. It dissolves in H_2SO_4 to a reddish-yellow, strongly fluorescent soln., whilst in HNO_3 the soln. is yellow, changing to pink when kept. The yellow soln. in alkali is not fluorescent at first, but becomes so when kept for a few mins., the fluorescence gradually fading on exposure to air as the reddish-violet colour due to formation of aloe-emodin appears. The formation of aloe-emodin by aerial oxidation of the anthranol in alk. soln. was confirmed by its isolation and conversion into its Ac derivative, m. p. 176—177°. When the anthranol (0·29 g.) in Ac_2O (2 c.c.) was treated with boroacetic anhydride (0·29 g.), no colour developed in the cold, but 15 secs.' warming on the water-bath caused appearance of an intense purple colour and separation of a dark insol. solid. An attempt to isolate this substance was unsuccessful. When the anthranol was methylated with Me_2SO_4 and K_2CO_3 in acetone in an atm. of N, a yellow resin was obtained which could not be crystallised. It gave rhein dimethyl ether when oxidised with $KMnO_4$.

Dihydroaloe-emodinanthranol.—Aloe-emodinanthranol (3 g.), Pd–norite (10%; 1 g.), and H_2O (40 c.c.) were mixed in the reduction vessel and, after displacement of the air by H, KOH aq. (20%; 10 c.c.) was introduced. The absorption of H (240 c.c.; calc., 248 c.c.) was slow and ceased after 22 hrs. The sparingly sol. K salt, which had separated, was collected, washed with AcOK soln., and dissolved in much hot H_2O, whence acid pptd. a solid (0·9 g.). *Dihydroaloe-emodinanthranol* crystallised from AcOH or AcOEt in glistening, golden plates with a bronze reflex, m. p. 180° (Found: C, 69·8; H, 5·8. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%). The dihydroanthranol gives with H_2SO_4 containing SeO_2 a port-wine colour, changing to purple and then to green on warming. Attempts to prepare a cryst. Ac derivative were unsuccessful.

Oxidation of Barbaloin with Ferric Chloride.—A mixture of barbaloin (10 g.), $FeCl_3$ (50 g.), and H_2O (150 c.c.) was heated under reflux at 115° for 15 mins. and then at 125° for 6 hrs. The brown solid (6·7 g.), which separated from the cooled solution, was collected, dried, and extracted with boiling C_7H_8, and on cooling aloe-emodin crystallised (yield 70%)—identified by m. p. 218° and by conversion into Ac derivative, m. p. 176—177° (Found : C, 63·3; H, 3·9. Calc. for $C_{21}H_{16}O_8$: C, 63·6; H, 4·0%).

Oxidation of Penta-acetyltribromobarbaloin (Penta-acetyltribromonorbarbaloin) with Chromic Anhydride.—To a soln. of the Ac derivative (5 g.) in Ac_2O (30 c.c.), CrO_3 (8 g.) in AcOH was gradually added, the oxidation proceeding readily at 80—90°. On standing in the cold, a yellow cryst. solid (0·2 g.) separated slowly. This was collected and repeatedly recryst. from AcOH–Ac_2O, in which it was very sparingly sol. *Triacetyltetrabromoaloe-emodin* separated in yellow nodules, decomp. 291—292° (Found : C, 35·4; H, 1·9. $C_{21}H_{12}O_8Br_4$ requires C, 35·4; H, 1·7%). Tetrabromoaloe-emodin, prep. by hydrolysis of the Ac_3 derivative, crystallised from $CHCl_3$ in bright red prisms, m. p. 272° (Léger, m. p. 264—266°) (Found : C, 30·7; H, 1·2; Br, 54·5. Calc. for $C_{15}H_6O_4Br_4$: C, 30·7; H, 1·0; Br, 54·6%). The original AcOH mother-liquor from which the Ac_3 derivative had separated gave on dilution with H_2O a yellow solid (1·8 g.). From this a further quantity (0·1 g.) of the Br_4-derivative was separated by crystn. from AcOH, the mother-liquor yielding a small amount of a colourless solid crystallising in well-defined plates, m. p. 272°. Sufficient was not obtained for analysis.

Action of Piperidine on Tribromobarbaloin (Tribromonorbarbaloin) Pentamethyl Ether.—A mixture of the Me_5 ether (1·8 g.) and piperidine (3·6 c.c.) was heated on the water-bath for 1 hr., an orange solution resulting. The solid obtained by addition of H_2O and acidification was collected, ground with NaOH aq., and filtered off, the residue (A) being well washed with H_2O. Acidification of the alk. filtrate pptd. a phenol (0·135 g.), a further quantity (0·2 g.) being obtained when the solid (A) (1·3 g.) was heated with piperidine (3 c.c.) for 3 hrs. on the water-bath. *Tribromobarbaloin trimethyl ether* crystallised from C_7H_8 in a mixture of yellow plates and needles, the former separating on rapid cooling and slowly passing into the latter; decomp. 260° after sintering at 250°. The two fractions of the ether were analysed [Found : C, 38·2, 38·4; H, 3·5, 3·4; Br, 39·8, 39·6; OMe, 15·4, 13·4. $C_{16}H_{12}O_4Br_3(OMe)_3$ requires C, 37·9; H, 3·5; Br, 39·9; OMe, 15·5%]. A cryst. Ac derivative could not be prepared.

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