The Biosynthesis of Phenols. Part XXI.[1] The Molecular Structure of Arugosin, a Metabolite of a Wild-type Strain of *Aspergillus rugulosus*

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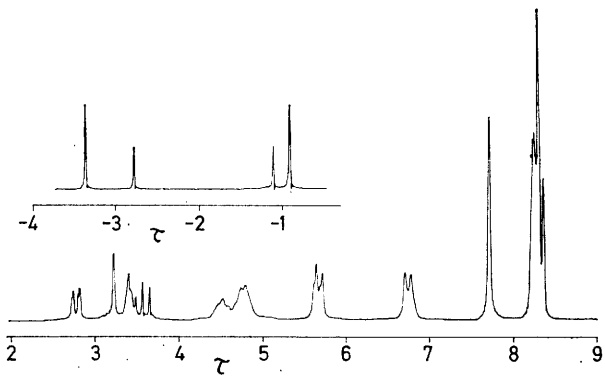
It has been established that arugosin, $C_{25}H_{28}O_6$, a metabolic product of a strain of *Aspergillus rugulosus*, is a mixture of two substituted dibenz[*b*,*e*]oxepins with the structures (IX) and (X). The nature and orientation of substituents in arugosin and in the single tri-*O*-methyl derivative, a substituted benzophenone (V), was established by degradation and by the ^{1}H n.m.r. and mass spectra of the compounds themselves and of their transformation products.

OUR interest in the use of mutants for the elucidation of the biosynthesis of secondary metabolites of fungi [2,3] has led us to investigate the molecular structure of an unusual metabolite of *Aspergillus rugulosus* which we have called arugosin. This compound is produced by the wild-type strain of *A. rugulosus* which has been used for subsequent mutation experiments. Earlier papers in this series [4] have described the novel phenolic compounds derived from several mutants of this wild-type and have discussed the genetical relationships of particular strains.[5]

Arugosin was isolated from the mycelium of *A. rugulosus* (I.M.I. 84338) and separated from other metabolites by counter-current distribution followed by chromatography on silica gel. This yielded an optically inactive yellow oil, $C_{25}H_{28}O_6$, which gave a mono-oxime and a bis-3,5-dinitrobenzoate, both crystalline. Arugosin was highly sensitive to the action of acid which converted it into a complex mixture of products. Although, at the outset of the investigation, only a limited interpretation of the ^{1}H n.m.r. spectrum (Figure) was possible, taken with earlier evidence of isoprenyl residues in metabolites of *A. rugulosus*,[4b] and the formation of 1·6 mol. of acetone on ozonolysis, the data did suggest (Table) that the molecule contained the two substituent groupings: $Me_2C{=}CH{-}CH_2{-}O{-}Ar$ and



^{1}H N.m.r. spectrum of arugosin at 100 MHz

[1] Part XX, J. S. Davies, V. H. Davies, and C. H. Hassall, *J. Chem. Soc.* (*C*), 1969, 1873.

[2] C. H. Hassall, 'Biogenesis of Antibiotic Substances,' ed. Z. Vanek and Z. Hostalek, Czechoslovak Academy of Sciences, Prague, 1965, p. 51.

[3] R. F. Curtis, P. C. Harries, C. H. Hassall, and J. D. Levi, *Biochem. J.*, 1964, **90**, 43.

[4] (*a*) J. A. Ballantine, C. H. Hassall, and G. Jones, *Tetrahedron Letters*, 1964, **49**, 3739; (*b*) J. A. Ballantine, C. H. Hassall, and G. Jones, *J. Chem. Soc.*, 1965, 4672; (*c*) J. A. Ballantine, C. H. Hassall, B. D. Jones, and G. Jones, *Phytochemistry*, 1967, **6**, 1157; (*d*) J. A. Ballantine, C. H. Hassall, and B. D. Jones, *ibid.*, 1968, **7**, 1529; (*e*) J. A. Ballantine, V. Ferrito, C. H. Hassall, and (in part) V. I. P. Jones, *J. Chem. Soc.*, 1969, 56.

[5] C. H. Hassall and K. Lawrence, *J. Gen. Microbiol.*, 1964, **35**, 483.

$Me_2C{=}CH{-}CH_2{-}Ar$. In addition there was evidence of the following groupings: Me–Ar, H–Ar, *ortho*-H_2Ar, and two chelated and one non-chelated OH (both exchangeable). Evidence that the non-chelated hydroxy-group was alcoholic was obtained from the ^1H n.m.r. spectrum of the diacetate of arugosin. Two acetate absorptions were observed, at τ 7·73 (ArOAc) and 8·11 (alcoholic OAc; *cf.* τ 8·03 for t-butyl acetate,[6] τ 7·97 for ethyl acetate[7]). It appeared likely that this alcoholic hydroxy-group was part of the function ·CH(OH). The signal for the single proton, τ 3·46, sharpened on deuteriation and was deshielded (shift of 1·12 p.p.m.) on acetylation of the hydroxy-group.

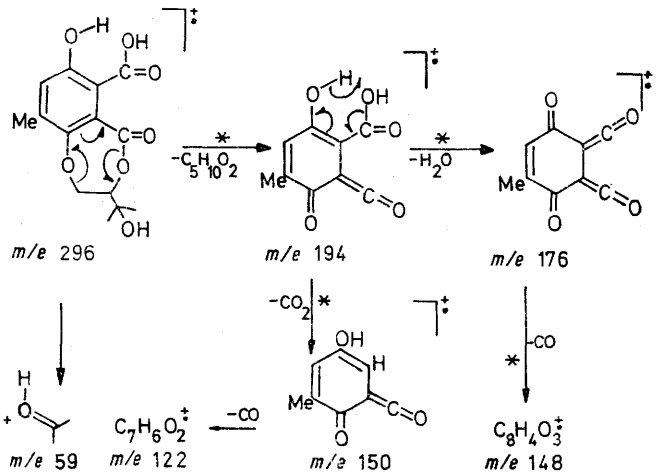
The nature and orientation of substituents in one of the aromatic nuclei of arugosin was rigorously established through degradation with hydrogen peroxide in alkali. This gave three crystalline phenolic acids. The structure (I) of the simplest compound, $C_9H_8O_6$, was suggested by the positive fluorescein test and the formation of an anhydride, the ^1H n.m.r. spectrum of which included signals at τ −1·13 (s, 2H) for two chelated hydroxy-groups and at τ 7·65 (3H, s) for an aryl methyl group. It was confirmed by comparison with material synthesised from toluene-2,5-quinone, is a 3,4-dicyano-2,5-dihydroxytoluene by a procedure similar to that employed for the preparation of 3,6-dimethoxyphthalic anhydride from *p*-benzoquinone.[8] The structure of the second product of oxidation, $C_{14}H_{16}O_7$, was deduced from its spectroscopic characteristics. There were two i.r. carbonyl bands at 1740 (conjugated lactone) and 1670 (chelated carboxy-group) cm.$^{-1}$; the mass spectrum provided good evidence, in particular in terms of the analysis of metastable ions, for the fragmentation pattern shown in Scheme 1. The ^1H n.m.r. spectrum was in accord with the structure (II). Moreover, it defined the position of the methyl substituent. The change (0·75 p.p.m.) in the chemical shift of the single aromatic proton when the phenolic hydroxy-group was converted into the phenolate ion was in the range (0·60—0·84).[9] This established the *ortho*-relationship between this proton and the phenolic hydroxy-group. The structure (III) of the third product of oxidation followed from a comparison of its spectroscopic properties with those of the other two acids. Presumably, this dicarboxylic acid was the precursor of the compound (II).

The nature of the second nucleus, B, of arugosin was suggested by the properties of the tri-*O*-methyl derivative and by the observation that fusion of arugosin with sodium hydroxide gave resorcinol and isovaleric acid. Although the latter result had to be interpreted with caution in view of the well recognised possibility of hydroxylation of phenols under alkali-fusion conditions,[10,11] taken literally, and this is allowed by

^1H N.m.r. assignments for arugosin and derivatives (τ values; solvent $CDCl_3$)

Assignments	No. of protons	Multiplicity (*J* in Hz)	Arugosin (IX) + (X)	Tri-*O*-methyl arugosin (V)	Anhydroarugosin (XIII)	Borohydride product (XVII)
Chelated ArOH	1 *	s	(−3·37, −2·78)		−2·48	
Chelated ArOH	1 *	s	(−1·09, −0·87)			
ArCHO	1	s		0·06	−0·74	
ArOH	3 *	s				2·70
ArH	1	d(8)	2·76	3·06	2·50	3·14
ArH	1	s	3·19	3·32	2·85	3·48
ArH	1	d(8)	(3·41, 3·61)	3·59	3·22	3·70
$Ar_2CH{\cdot}O$	1	s				3·29
$ArCH(OH){\cdot}O$	1	d(5)	3·46			
$ArO{\cdot}CH_2{\cdot}CH{=}$	1	m	4·48	4·59	4·60	4·4—5·0
$ArCH_2{\cdot}CH{=}$	1	m	4·73	4·84	4·60	4·4—5·0
$ArCH_2{\cdot}O$	2	m †				4·4—5·0
$ArCH(OH){\cdot}O$	1 *	d †(5)	5·00			
$ArO{\cdot}CH_2{\cdot}CH{=}$	2	d(7)	5·66	5·71	5·50	5·72
$ArCH_2{\cdot}CH{=}$	2	d(8)	6·74	6·82	6·64	6·77
ArOMe	3	s		6·41, 6·50, 6·63		
ArMe	3	s	7·68	7·77	7·56	7·71
$CH{=}CMe_2$	12	d(7)	8·25	8·31	8·32	8·26

* Exchangeable. † Broad.

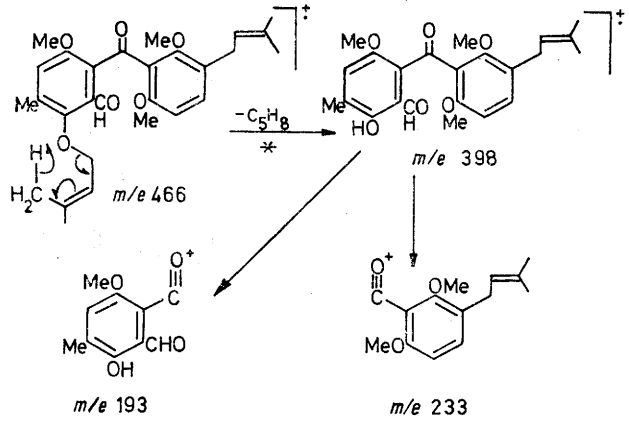


SCHEME 1 Fragmentation processes in the mass spectrum of compound (II)

[6] Varian N.M.R. Spectra Catalog, 1962, Spectrum No. 141.
[7] Varian N.M.R. Spectra Catalog, 1962, Spectrum No. 79.
[8] J. Thiele and F. Günther, *Annalen*, 1906, **349**, 45.
[9] R. J. Highet and P. F. Highet, *J. Org. Chem.*, 1965, **30**, 902.
[10] L. Barth and J. Schreder, *Ber.*, 1879, **12**, 417, 503.
[11] R. Lemberg, *Ber.*, 1929, **62**, 592.

analogous cases,[12,13] it favoured a structure for arugosin in which the second isopentenyl residue in the molecule was attached to the resorcinol nucleus itself, in a manner which permits the existence of an '*ortho* pair' of hydrogen atoms. Furthermore, the probable mechanism of the reaction giving rise to isovaleric acid required that the isopentenyl residue was *ortho* to a free phenolic hydroxy-group.[14] With this restriction of the orientation of the isopentenyl group to two alternatives (IVa or b), the spectroscopic properties of the tri-*O*-methyl derivative, $C_{28}H_{34}O_6$, a colourless, crystalline compound prepared by mild, Robertson [15] methylation of arugosin, made it possible to assign the structure (IVa) to the nucleus B, and (V) to the methylation product itself.

The ^{1}H n.m.r. signals of the tri-*O*-methyl derivative are summarised in the Table. A singlet at τ 0·06 (unaffected by the addition of deuterium oxide) was attributed to a formyl group. The presence of an i.r. band at 1705 cm.$^{-1}$ supported this assignment. Apart from this formyl and the three methoxy-groups, all aryl-linked, the ^{1}H n.m.r. spectrum indicated the presence of three protons, two isopentenyl groups, and one methyl group, in positions similar to those in arugosin itself. This evidence, taken in conjunction with the molecular formula, accounted for all but two atoms, C and O, and two points of substitution on two aromatic nuclei; it suggested that the tri-*O*-methyl derivative was a benzophenone. This was supported by the mass spectrum. An initial fragmentation process yielded an abundant ion, *m/e* 398, by the expulsion of the unit C_5H_8 from the oxygen-linked isopentenyl group. A commonly observed six-membered rearrangement process was involved.[16,17] Subsequent fragmentations



SCHEME 2 Fragmentation processes in the mass spectrum of compound (V)

of the ion *m/e* 398 were characteristic of benzophenones.[18] The cleavages giving rise to abundant acylium ions, *m/e* 233 and 193 were in accord with the formulation (V) of the tri-*O*-methyl derivative (Scheme 2). The differences between the ^{1}H n.m.r. spectra of arugosin and the tri-*O*-methyl derivative established that the latter included a formyl group which was masked in arugosin through hemiacetal formation involving a phenolic hydroxy-group. This could occur to give a compound with two chelated hydroxy-groups with the substitution pattern of ring B as in (IVa), but not (IVb).

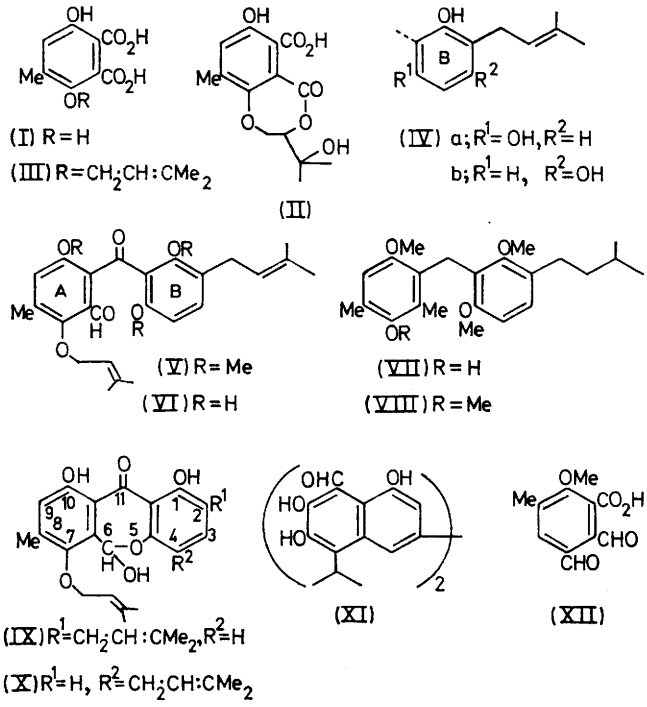
Final proof of the orientation of the substituents came from a comparison of the substituted diphenylmethane (VIII) prepared by an unequivocal synthesis,[19] with the compound derived from the tri-*O*-methyl derivative of arugosin by hydrogenation, followed by methylation. The two products were identical. This established, unambiguously, the structure (V) for the tri-*O*-methyl derivative. The unusually high τ-values of the ^{1}H n.m.r. three-proton singlets for the three methoxy-groups in the compound (V), 6·41, 6·50, and 6·63, were attributed to the 'molecular crowding' arising from substitution of bulky groups in the 2-, 2′-, 6-, and 6′-positions. This would be expected to result in a conformation with the aromatic rings non-coplanar and so arranged that the shielding effects of the bridge carbonyl group and of these rings, were more significant. We have observed similar effects in related 2,2′,6,6′-substituted benzophenones.

The ^{1}H n.m.r. spectrum of our sample of arugosin, in deuteriochloroform (Figure), included features that indicated the presence of a mixture of two components. There were four signals in the region τ −0·8 to −3·4, attributed to chelated hydroxy-groups; they integrated in pairs for one proton per pair but did not vary in position or relative intensity over the temperature range 20—70°. This made it unlikely that an equilibrium mixture of tautomers was involved. In addition, there were two doublets (both with J 8 Hz) at τ 3·41 and 3·61 which integrated for a total of one proton. In each of these three cases, the individual signals comprising the pair were in the ratio 2 : 1 by integration. Moreover, the spectrum of a solution in deuteriobenzene showed further evidence for a two-component mixture. The signal at τ 6·74 (2H, J 8 Hz) in the spectrum of a solution in deuteriochloroform, now appeared as two doublets τ 6·54 and 6·70 (both J 8 Hz) integrating as a pair for two protons but, individually, again in the ratio 2 : 1. A similar separation occurred for the signal at τ 5·00.

These properties suggested a 2 : 1 mixture of isomers arugosin A and arugosin B, with the structures (IX) and (X) respectively. They accounted for the formation of of the single tri-*O*-methyl-derivative (V) on treatment with methyl iodide and potassium carbonate. We

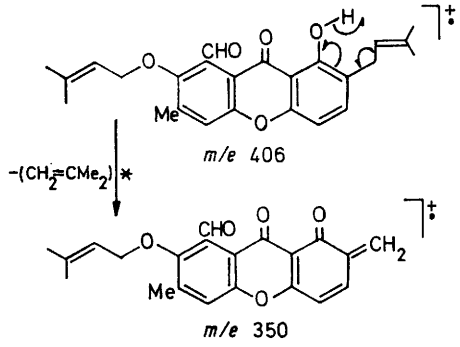
[12] E. Spath and K. Klager, *Ber.*, 1934, **67**, 859.
[13] B. C. L. Weedon, 'Techniques of Organic Chemistry,' ed. A. Wensberger, Interscience, New York, 1963, vol. XI, part II, ch. XII.
[14] P. Yates and G. H. Stout, *J. Amer. Chem. Soc.*, 1958, **80**, 1691.
[15] A. Robertson, R. Robinson, and A. Struthers, *J. Chem. Soc.*, 1928, 1455.
[16] N. S. Wulfson, V. I. Zaretski, and V. G. Zyakoon, *Dodlady Akad. Nauk S.S.S.R.*, 1964, **155**, 1104.
[17] E. Ritchie, W. C. Taylor, and J. S. Shannon, *Tetrahedron Letters*, 1964, **23**, 1437.
[18] J. A. Ballantine and C. T. Pillinger, *Org. Mass Spectrometry*, 1968, **1**, 425.
[19] E. R. Catlin and C. H. Hassall, unpublished work.

favour the structure (X) for the major component. The signals τ −2·78 and −1·09 are assigned to the protons of the chelated C-1 and C-10 hydroxy-groups in arugosin B, rather than A (assigned the corresponding signals τ −3·37 and −0·87) since the compound formulated as (X) has these protons in a more similar molecular



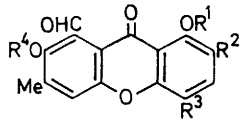
environment than (IX). Evidently, arugosin A and B may be regarded as the products formed by neighbouring-group interactions between a 2-formyl- and either 2′- or 6′-hydroxy-groups of a substituted benzophenone. There is some similarity to the interactions of formyl and hydroxy-substituents in gossypol [20] (XI) and gladiolic acid [21] (XII).

With the structures of the two forms of arugosin defined as 1,6,10-trihydroxy-2-isopent-2-enyl-7-isopent-2-enyloxy-8-methyldibenz[*b*,*e*]oxepin-11-one (IX), and the isomer (X), it became possible to account for certain reactions which had been observed during the initial stages of the investigation. During attempts to obtain pure arugosin by chromatography on activated silica gel, two light-yellow crystalline compounds, anhydroarugosin ($C_{25}H_{26}O_5$) and deisopentenylanhydroarugosin ($C_{20}H_{18}O_5$) were formed. The u.v. spectra of both compounds were characteristic of xanthones.[22] The ^1H n.m.r. spectrum of anhydroarugosin (Table) included evidence of a formyl group; this was replaced by a methyl group in both the crystalline products, $C_{25}H_{32}O_4$ and $C_{20}H_{22}O_4$, formed on hydrogenation. Of the two possible structures for xanthones derived from arugosin through loss of the elements of water, we favour (XIII) for anhydroarugosin. The alternative (XIV) with the 4-isopentenyl substituent was excluded by a positive Gibbs test [23] and the evidence, from the mass spectrum, that electron-induced fragmentation involved the formation of a significant ion at *m/e* 350 (*M* − 56). This indicated that the fragment C_4H_8 has been eliminated with hydrogen transfer (Scheme 3). As in the related

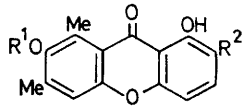


SCHEME 3 Mode of formation of an *M* − 56 ion in the mass spectrum of compound (XIII)

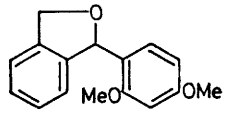
case of harongin anthrone [17] we attribute this easy elimination to the intermediacy of a six-membered transition state involving an adjacent hydroxy-group. This was not consistent with the alternative formulation (XIV). The structure (XV) of deisopentenylanhydroarugosin follows from similar arguments, based on the spectra of its products of methylation (XVI) and of hydrogenation (XVII).



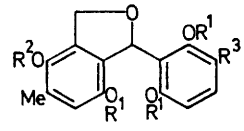
(XIII) $R^1 = R^3 = H$, $R^2 = R^4 = CH_2{\cdot}CH{:}CMe_2$
(XIV) $R^1 = R^2 = H$, $R^3 = R^4 = CH_2{\cdot}CH{:}CMe_2$
(XV) $R^1 = R^3 = R^4 = H$, $R^2 = CH_2{\cdot}CH{:}CMe_2$
(XVI) $R^1 = R^4 = Me$, $R^3 = H$, $R^2 = CH_2{\cdot}CH{:}CMe_2$
(XVII) $R^1 = R^3 = R^4 = H$, $R^2 = CH_2{\cdot}CH_2{\cdot}CHMe_2$



(XXII) $R^1 = R^2 = CH_2{\cdot}CH_2{\cdot}CHMe_2$
(XXIII) $R^1 = H$, $R^2 = CH_2{\cdot}CH_2{\cdot}CHMe_2$



(XVIII)



(XIX) $R^1 = H$, $R^2 = R^3 = CH_2{\cdot}CH{:}CMe_2$
(XX) $R^1 = Me$, $R^2 = H$, $R^3 = CH_2{\cdot}CH_2{\cdot}CHMe_2$
(XXI) $R^1 = Me$, $R^2 = R^3 = CH_2{\cdot}CH{:}CMe_2$

When arugosin was treated with sodium borohydride in methanol, reduction took place readily to yield a single product, $C_{25}H_{30}O_5$. The n.m.r. spectrum of this

[20] E. W. Scheiffele and D. A. Shirley, *J. Org. Chem.*, 1964, **29**, 3617.
[21] J. F. Grove, *Biochem. J.*, 1952, **50**, 648.
[22] R. P. Mull and F. F. Nord, *Arch. Biochem. Biophys.*, 1944, **4**, 419.
[23] F. E. King, T. J. King, and L. C. Manning, *J. Chem. Soc.*, 1957, 563.

compound (Table), and that of its tri-*O*-methyl derivative, in particular the characteristic broad singlet (1H, τ 3·29) due to the methine proton and the signals (2H, τ 4·8) due to the group ArCH_2·O which were observed in the spectra of these and the related compound [24] (XVIII), left no doubt that it was the substituted phthalan (XIX). A similar product (XX) was formed when the tri-*O*-methyl derivative of arugosin was hydrogenated under mild conditions.

The formation, from arugosin, of the phthalan and of the tri-*O*-methyl derivative indicated that the forms (IX) and (X) were readily converted into the single benzophenone (VI), presumably under the mildly basic conditions which were employed in both cases. However, there was no evidence to suggest that in neutral media the forms (IX) and (X) were in equilibrium.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage microscope. U.v. spectra were measured with a Unicam SP 800 spectrophotometer. I.r. spectra were determined with a Perkin-Elmer 257 spectrophotometer. ^{1}H N.m.r. spectra were obtained at 60 MHz with a Perkin-Elmer R10 instrument and at 100 MHz with a Varian HA100 instrument. Mass spectra were measured at 70 ev with an A.E.I. MS-9 spectrometer. All the molecular formulae quoted for ions were established by accurate mass measurement. R_F Values refer to thin-layer chromatograms as previously described.[4c]

Extraction and Purification of Arugosin.—Wild-type *Aspergillus rugulosus*, I.M.I. strain No. 84338, was grown from a spore suspension for 15 days at 25° on a low-nitrogen medium.[5] The stationary cultures were in batches of 800 flat-sided bottles (*ca.* 1 l. capacity) each containing 200 ml. of medium. The mycelium, after separation from the culture fluid with a wire mesh strainer, was macerated in a blender with distilled water (100 ml. for 5 bottles) and the macerate was extracted with ether (250 ml. for 5 bottles). Concentration of the ether solution from 800 bottles *in vacuo* yielded a dark brown viscous residue (34 g.). Aliquot portions of the residue (10—15 g.) were distributed equally between the first six tubes of a 200-tube automatic countercurrent distribution instrument, (H.O. Post Scientific Instrument Co.) and subjected to 600 transfers, with 10 ml. phases of light petroleum–methanol–water (8 : 10 : 1 v/v). Tubes 70—110 yielded impure arugosin as a light yellow syrup (400—600 mg.; R_F 0·78). This was subjected to preparative layer chromatography on Kieselgel G plates (200 mg. on each 50 × 20 × 0·1 cm. plate) with light petroleum–ethyl acetate (72 : 28 v/v) as eluant. The light yellow band R_F 0·75 was collected; the metabolite was eluted with ethyl acetate. Evaporation of the solvent *in vacuo* furnished *arugosin* as a viscous, yellow oil (400—600 mg.) [Found: C, 70·8; H, 6·9%; *M* (mass spectrometry), 424·1886 ± 0·0020. $C_{25}H_{28}O_6$ requires C, 70·7; H, 6·65%; *M*, 424·1886], $\nu_{max.}$ ($CHCl_3$) 3395 (OH) and 1735 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 227, 280, and 365 nm. (log ε 4·32, 3·97, and 3·86), $\lambda_{max.}$ (EtOH–NaOH) 241, 272, 384, and 427 nm. (log ε 4·58, 4·27, 3·94, and 3·93).

Oxime of Arugosin (with H. Link).—Arugosin (140 mg.) in ethanol (7 ml.) was treated with a solution of hydroxylamine hydrochloride (375 mg.) in water (1·5 ml.) and sodium hydroxide solution (10%; 1·5 ml.) for 24 hr. at 20°. The *oxime* was extracted into ether and obtained as colourless microcrystals (90 mg.) from chloroform–pentane, m.p. 165—167° (decomp.) (Found: C, 68·3; H, 6·7; N, 3·2; O, 21·8. $C_{25}H_{29}NO_6$ requires C, 68·3; H, 6·7; N, 3·1; O, 21·8%), $\nu_{max.}$ (KBr) 3600 (OH) and 1680 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 221, 288, and 309 nm. (log ε 4·5, 3·7, and 3·8).

Bis-3,5-dinitrobenzoate of Arugosin.—Arugosin (497 mg.) was treated with 3,5-dinitrobenzoyl chloride in pyridine at 20° for 48 hr. The *bis-3,5-dinitrobenzoate* was obtained as bright yellow prisms from benzene–light petroleum (525 mg.), m.p. 175—177° (Found: C, 57·7; H, 4·3; N, 6·8. $C_{39}H_{33}N_4O_{16}$ requires C, 57·6; H, 4·0; N, 6·9%), $\nu_{max.}$ (KBr) 1755 (CO), 1620, and 1545 (NO_2) cm.$^{-1}$.

Treatment of the bis-3,5-dinitrobenzoate (555 mg.) with ozone furnished a steam-distillate from which acetone 2,4-dinitrophenyl hydrazone (254 mg., 1·57 mole) was isolated.

Diacetate of Arugosin.—Arugosin (153 mg.) was shaken with acetic anhydride (3·5 ml.) and anhydrous sodium acetate (1·5 g.) at 20° for 56 hr. The products were poured into excess of potassium hydrogen carbonate solution, left for 8 hr., and extracted into chloroform. The resultant mixture of products was purified by preparative layer chromatography on Kieselgel G (20 × 20 × 0·1 cm.) with chloroform as eluting solvent. Extraction of the light yellow band (R_F 0·8) with chloroform, furnished the *diacetate* (28 mg.) as a pale-yellow viscous liquid [Found: *M* (mass spectrometry), 508·2106 ± 0·0025. $C_{29}H_{32}O_8$ requires *M*, 508·2097], $\nu_{max.}$ ($CHCl_3$) 1762 (CO), 1715 (CO), and 1620 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 220, 232 infl., 267 infl., 303, and 378 nm. (log ε 4·28, 4·15, 3·83, 4·03, and 3·30), τ $CDCl_3$ —2·27 (1H, s, chelated ArOH, exchangeable), 2·34 (1H, s, ArC*H*(OAc)·O), 2·72 (1H, d, *J* 8 Hz, ArH), 3·02 (1H, s, ArH), 3·60 (1H, d, *J* 8 Hz, ArH), 4·47 (1H, m, ArO·CH_2·C*H*=), 4·73 (1H, m, ArCH_2·C*H*=), 5·63 (2H, d, *J* 7 Hz, ArO·CH_2·CH=), 6·73 (2H, d, *J* 7 Hz, ArCH_2·CH=), 7·65 (3H, s, ArMe), 7·73 (3H, s, ArO·COMe), 8·11 (3H, s, CH(·O·CO*Me*)·O), 8·24 (6H, d, *J* 7 Hz, CH=CMe_2), and 8·34 (6H, d, *J* 7 Hz, CH=CMe_2).

Oxidation of Arugosin with Alkaline Hydrogen Peroxide.—Arugosin (3·52 g.) was dissolved in 2N-sodium hydroxide (250 ml.) and hydrogen peroxide (30%; 50 ml.) was added. After 56 hr. at 40° the solution was filtered, acidified with dilute hydrochloric acid, and extracted with ether. Acidic products were extracted into sodium hydrogen carbonate solution (10%; 2 × 300 ml.), from which they were recovered by acidification and extraction into ether (2 × 1000 ml.). The mixture of acidic oxidation products obtained as a brown viscous residue (660 mg.) from the ether extract was chromatographed on silica gel (45 g.; 200—300 mesh, Koch-Light) with gradient elution.

Elution with pentane–ether (85 : 15 v/v) gave fractions which yielded a colourless solid (75 mg.) upon evaporation. Recrystallisation from benzene gave the $C_{14}H_{16}O_6$ oxidation *product* (III), colourless microcrystals (42 mg.), m.p. 144—146°, which gave a positive fluorescein test (Found: C, 60·3; H, 6·05. $C_{14}H_{16}O_6$ requires C, 60·0; H, 5·75%), $\nu_{max.}$ (KBr) 3400 (OH), 2600br (CO_2H), and 1665 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 215, 247, and 333 nm. (log ε 4·20, 3·75, and 3·68), τ ([$^2H_5$]pyridine) —1·40br (3H, s, exchangeable, OH), 2·92 (1H, s, ArH), 4·45br (1H, m, CH_2·C*H*=), 4·94 (2H, d, *J* 7 Hz, ArO·CH_2), 7·64 (3H, s, ArMe), and 8·44 (6H, s, Me_2C=).

[24] V. H. Davies, Ph.D. Thesis, University of Wales, 1968.

Elution with pentane–ether (75 : 25 v/v) gave fractions which yielded a second colourless solid (241 mg.) upon evaporation. Recrystallisation from benzene gave the $C_9H_8O_6$ oxidation *product* (I), colourless microcrystals (235 mg.), m.p. 172—174°, which gave a positive fluorescein test [Found: C, 48·3; H, 4·3; O, 47·0%; *M* (mass spectrometry), 212. $C_9H_8O_6$,0·5H_2O requires C, 48·8; H, 4·1; O, 47·1%. $C_9H_8O_6$ requires *M*, 212], $\nu_{max.}$ (KBr) 3440 (OH), 3350 (OH), 3100br (CO_2H), 1705 (CO), and 1660 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 215 and 348 nm. (log ε 4·21 and 3·70), τ −3·1 (4H, s, exchangeable, OH), 2·91 (1H, s, ArH), and 7·70 (3H, s, ArMe). When this product (42 mg.) was sublimed (130°/0·05 mm.) it gave the corresponding *anhydride* as bright yellow microcrystals (29 mg.), m.p. 182—184° (Found: C, 55·9; H, 3·5. $C_9H_6O_5$ requires C, 55·7; H, 3·1%), $\nu_{max.}$ (KBr) 3340 (OH), 2350br (OH), and 1805 and 1735 (anhydride CO) cm.$^{-1}$, $\lambda_{max.}$ (Me_2SO) 220, 244, 267, and 374 nm. (log ε 4·12, 4·15, 3·74, and 3·74), τ (Me_2SO) −1·13 (2H, s, exchangeable, OH), 2·88 (1H, s, ArH), and 7·65 (3H, s, ArMe), τ (Me_2SO–NaOH) 3·50 (1H, s, ArH).

Elution with pentane–ether (60 : 40 v/v) gave fractions which yielded a third colourless solid (82 mg.). Recrystallisation from ethyl acetate gave the $C_{14}H_{16}O_7$ oxidation *product* (II) as colourless microcrystals (64 mg.), m.p. 197—199° [Found: C, 56·6; H, 5·5%; *M* (mass spectrometry), 296. $C_{14}H_{16}O_7$ requires C, 56·8; H, 5·4%; *M*, 296.], $\nu_{max.}$ (KBr) 3440 (OH), 2440br (CO_2H), 1740 (lactone CO), and 1670 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 214, 253, and 327 nm. (log ε 4·36, 3·67, and 3·68), τ (Me_2SO) 3·05 (1H, s, ArH), τ (Me_2SO–NaOH) 3·80 (1H, s, ArH), τ ([$^2H_5$]-pyridine) −1·88 (2H, s, exchangeable, OH), 2·93 (1H, s, ArH), 5·20 (1H, s, OH), 5·30 (2H, d, *J* 7 Hz, ArO·C*H*$_2$·CH=), 5·58 (1H, t, *J* 7 Hz, ArO·CH$_2$·C*H*), 7·78 (3H, s, ArMe), 8·44 (3H, s, MeCO), and 8·52 (3H, s, MeCO), *m/e* 296(29%), 278(8), 263(7), 252(11), 195(50), 194(100), 191(21), 190(21), 177(25), 176(66), 151(45), 150(42), 148(21), 122(17), 85(16), 71(27), 59(88), 53(16), 44(42), 43(52), 41(20), and 39(17), *m** 261·1(278^2/296), 166·8(178^2/190), 160·7(177^2/195), 159·6(176^2/194), 127·1(194^2/296), 124·5(148^2/176), 116·0(150^2/194), 100·5(122^2/148), and 99·2(122^2/150).

3,6-*Dihydroxy*-4-*methylphthalic Anhydride*.—3,4-Dicyano-2,5-dihydroxytoluene [25] (10 g.) was benzylated in the usual way to give 2,5-*dibenzyloxy*-3,4-*dicyanotoluene* as colourless needles from ethanol (4·5 g.), m.p. 138° (Found: C, 77·9; H, 5·3; N, 7·6. $C_{23}H_{18}O_2N_2$ requires C, 77·9; H, 5·1; N, 7·9%).

2,5-Dibenzyloxy-3,4-dicyanotoluene (4·0 g.) was refluxed with potassium hydroxide solution (50%; 50 ml.) and ethanol (25 ml.) for 5 hr. After cooling and acidification with ice-cold 5N-sulphuric acid (100 ml.) the solution was maintained at 0° for 1 hr. Extraction with ethyl acetate furnished a pale yellow solid (1·7 g.) which, on crystallation from ethyl acetate, gave 3,6-*dibenzyloxy*-4-*methylphthalic anhydride* as long pale yellow needles (903 mg.), m.p. 162° (Found: C, 73·7; H, 5·1. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·85%), $\nu_{max.}$ (mull) 1820 and 1760 (anhydride CO) cm.$^{-1}$.

Catalytic hydrogenation of 3,6-dibenzyloxy-4-methylphthalic anhydride (412 mg.) followed by sublimation of the product yielded 3,6-*dihydroxy*-4-*methylphthalic anhydride* as yellow microcrystals (184 mg.), m.p. 182—184° (Found: C, 55·9; H, 3·5. $C_9H_6O_5$ requires C, 55·7; H, 3·1%), identical (i.r., u.v., and ^{1}H n.m.r. spectra and mixed m.p.) with the C_9 anhydride oxidation product from arugosin.

Fusion of Arugosin with Potassium Hydroxide (with H. Link).—Arugosin (1·93 g.) was fused with pulverised potassium hydroxide (20 g.) at 360° for 45 min. under nitrogen. The residue was separated in the usual way into a neutral fraction (67 mg.), a sodium hydrogen carbonate-soluble fraction (466 mg.), a 2N-sodium carbonate-soluble fraction (364 mg.), and a residual potassium hydroxide-soluble fraction (212 mg.).

The residue from the hydrogen carbonate extraction (466 mg.), which was shown by t.l.c. to contain at least seven phenolic compounds, was distilled at 60°/0·05 mm. The distillate further distilled at 25°/13 mm. to furnish isovaleric acid (59 mg.) (characteristic odour), $\nu_{max.}$ (film) 3570—3030 (CO_2H) and 1695 (CO) cm.$^{-1}$, τ ($CDCl_3$) −0·63 (1H, s, exchangeable, CO_2H), 7·8 (2H, d, *J* 7 Hz, OC·C*H*$_2$·CH), 8·75 (1H, m, CH$_2$·C*H*Me$_2$), and 9·0 (6H, d, *J* 7 Hz, CH*Me*$_2$). The *p*-bromophenacyl ester had m.p. and mixed m.p. 68·9°.

The residue from the sodium carbonate extraction (364 mg.), which was shown by t.l.c. to contain at least nine phenolic compounds, was chromatographed on silica gel (45 g.; 200—300 mesh) with gradient elution. Intermediate fractions gave a colourless solid (63 mg.; R_F 0·2) which after sublimation and recrystallisation from benzene–light petroleum yielded resorcinol as colourless needles, m.p. and mixed m.p. 112° (Found: C, 65·8; H, 5·4; O, 28·8. Calc. for $C_6H_6O_2$: C, 65·4; H, 5·5; O, 29·1%), identical (i.r., u.v., and mass spectra) with authentic resorcinol.

Reaction of Arugosin with Methyl Iodide.—Arugosin (100 mg.) was dissolved in a mixture of acetone (20 ml.) and methyl iodide (20 ml.). Anhydrous potassium carbonate (1·5 g.) was added and the mixture was stirred at room temperature for 18 hr. until methylation was complete (t.l.c.). Dry ether (150 ml.) was added, the carbonate was removed on glass fibre paper, and the solvents were removed *in vacuo* to yield a single product (R_F 0·4) as a colourless syrup. Trituration with ether gave the *tri*-O-*methyl derivative* (V) of arugosin as colourless microcrystals (84 mg.), m.p. 101° (from ether) [Found: *M* (mass spectrometry), 466·2355 ± 0·0022. $C_{28}H_{34}O_6$ requires *M*, 466·2355], $\nu_{max.}$ (KBr) 1705 (ArCHO) cm.$^{-1}$ (no OH absorption), $\lambda_{max.}$ (EtOH) 221, 262, and 337 nm. (log ε 4·41, 3·90, and 3·64), *m/e* 398 ($C_{23}H_{22}O_6$, 21%), 233 ($C_{14}H_{17}O_3$, 19%), and 193 ($C_{10}H_9O_4$, 16%).

Hydrogenation of the Tri-O-methyl Derivative of Arugosin.—(a) *Mild conditions*. The tri-*O*-methyl derivative (60 mg.) in dry ethanol (10 ml.) was shaken at 20° with 10% palladium–carbon (30 mg.) for 18 hr. under hydrogen. The product was purified by preparative layer chromatography on Kieselgel G as previously described. A major component (R_F 0·35) was separated from a minor component (R_F 0·75). The former was extracted with ethyl acetate to furnish the *tri*-O-*methylphthalan derivative* (XX) as a colourless solid (41 mg.), m.p. 107—109° [Found: *M* (mass spectrometry), 386·2093 ± 0·0010. $C_{23}H_{30}O_5$ requires *M*, 386·2093], $\nu_{max.}$ (KBr) 3380 (OH) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 232 and 286 nm. (log ε 4·30 and 3·74), τ ($CDCl_3$) 2·98 (1H, d, *J* 8 Hz, ArH), 3·24br (1H, s, O·CHAr$_2$), 3·46 (1H, d, *J* 8 Hz, ArH), 3·54 (1H, s, ArH), 4·80 (2H, ABm, *J* 12 Hz, ArCH$_2$·O), 6·38 (3H, s, ArOMe), 6·46 (3H, s, ArOMe), 6·58 (3H, s, ArOMe), 7·26 (2H, bm, ArC*H*$_2$·CH$_2$), 7·80 (3H, s, ArMe), 8·2—8·8 (3H, m, ArCH$_2$·C*H*$_2$·C*H*Me$_2$), and 9·06 (6H,

[25] W. K. Anslow and H. Raistrick, *Biochem. J.*, 1940, **34**, 1124.

d, J 7 Hz, CHMe_2), *m/e* 235 ($C_{14}H_{19}O_3$, 46%) and 179 ($C_{10}H_{11}O_3$, 37%).

(b) *More rigorous conditions.* The tri-*O*-methyl derivative of arugosin (60 mg.) in dry methanol (10 ml.) was shaken at 20° with 10% palladium–carbon (60 mg.) for 56 hr. under hydrogen. The product was purified by preparative layer chromatography on Kieselgel G as previously described. The major component (R_F 0·40) was extracted with ethyl acetate to furnish the *tri-O-methyldiphenylmethane derivative* (VII) as a colourless oil (38 mg.) [Found: *M* (mass spectrometry), 372·2297 ± 0·0018. $C_{23}H_{32}O_4$ requires *M*, 372·2300], $\lambda_{max.}$ (EtOH) 232 and 286 nm. (log ε 4·31 and 3·73), τ ($CDCl_3$) 3·06 (1H, d, J 8 Hz, ArH), 3·47 (1H, d, J 8 Hz, ArH), 3·50 (1H, s, ArH), 5·79br (1H, s, ArOH), 5·96 (2H, s, $ArCH_2Ar$), 6·31 (3H, s, ArOMe), 6·40 (3H, s, ArOMe), 6·48 (3H, s, ArOMe), 7·46br (2H, m, $ArCH_2{\cdot}CH_2$), 7·80 (3H, s, ArMe), 7·97 (3H, s, ArMe), 8·2—8·8 (3H, m, $ArCH_2{\cdot}CH_2{\cdot}CHMe_2$), and 9·05 (6H, d, J 7 Hz, CHMe_2), *m/e* 221 ($C_{14}H_{21}O_2$, 8%) and 165 ($C_{10}H_{13}O_3$, 22%).

The Tetra-O-methyldiphenylmethane Derivative (VIII).—The tri-*O*-methyldiphenylmethane derivative (30 mg.) was dissolved in a mixture of acetone (6 ml.) and methyl iodide (6 ml.). Anhydrous potassium carbonate (750 mg.) was added and the mixture was refluxed for 24 hr., until the reaction was complete (t.l.c.). Filtration and concentration *in vacuo* gave the *tetra-O-methyldiphenylmethane derivative* (VIII) as a colourless oil (26 mg.) [Found: *M* (mass spectrometry), 386·2457 ± 0·0018. $C_{24}H_{24}O_4$ requires *M*, 386·2456], τ ($CDCl_3$) 3·07 (1H, d, J 8 Hz, ArH), 3·49 (1H, d, J 8 Hz, ArH), 3·52 (1H, s, ArH), 5·99 (2H, s, $ArCH_2Ar$), 6·33 (3H, s, ArOMe), 6·43 (6H, s, 2 × ArOMe), 6·52 (3H, s, ArOMe), 7·48br (2H, m, $ArCH_2{\cdot}CH_2$), 7·77 (3H, s, ArMe), 7·92 (3H, s, ArMe), 8·2—8·8 (3H, m, $ArCH_2{\cdot}CH_2{\cdot}CHMe_2$), and 9·05 (6H, d, J 7 Hz, CHMe_2), identical (i.r., u.v., ^{1}H n.m.r. and mass spectra) of a synthetic sample of 3′-isopentyl-2′,3,6,6′-tetramethoxy-2,4-dimethyldiphenylmethane.[19]

The Action of Silica Gel on Arugosin.—Arugosin (1·24 g.) in ether (10 ml.) was applied to a column of active silica gel (Merck; <0·08 mm.) and subjected to gradient elution. The first few fractions contained two anhydro-compounds (536 mg.) which were rechromatographed on silica gel (200—300 mesh; Koch-Light) with 5% ether–light petroleum (b.p. 40—60°) as eluant.

Early fractions contained a yellow solid (127 mg.) which gave *anhydroarugosin* (XIII) as long needles, m.p. 134° (from benzene–light petroleum) [Found: C, 73·5; H, 6·8%; *M* (mass spectrometry), 406. $C_{25}H_{26}O_5$ requires C, 73·9; H, 6·5%; *M*, 406], $\nu_{max.}$ 3400 (OH), 1705 (CO), and 1640 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 237, 269, 295, and 384 nm. (log ε 4·19, 4·23, 3·85, and 3·39).

Later fractions contained a yellow solid (372 mg.) which furnished *deisopentenylanhydroarugosin* (XV) as microcrystals, m.p. 189—191° (from benzene) [Found: C, 71·4; H, 5·6%; *M* (mass spectrometry), 338. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·4%; *M*, 338], $\nu_{max.}$ 2720br (OH) and 1640 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 234, 247, 267, 300, and 408 nm. (log ε 3·31, 4·34, 4·34, 4·24, and 3·72), τ ($CDCl_3$) —3·32 (1H, s, exchangeable, OH), —2·80 (1H, s, exchangeable, OH), —1·39 (1H, s, ArCHO), 2·60 (1H, s, ArH), 2·64 (1H, d, J 8 Hz, ArH), 3·26 (1H, d, J 8 Hz, ArH), 4·72br (1H, m, $ArCH_2{\cdot}CH{=}$), 6·66 (2H, d, J 7 Hz, $ArCH_2$), 7·63 (3H, s, ArMe), 8·26 (6H, s, $Me_2C{=}$).

Hydrogenation of Anhydroarugosin.—Anhydroarugosin (100 mg.) in ethyl acetate (25 ml.) was shaken at 20° with 10% palladium–carbon (100 mg.) for 12 hr. under hydrogen. The product was purified by chromatography on silica gel (15 g.). Elution with light petroleum (b.p. 40—60°)–ether (95 : 5 v/v) yielded a yellow oil (40 mg.; R_F 0·90) which (from light petroleum) gave the *hydrogenation product* (XXII) as yellow needles, m.p. 46—48° (Found: C, 75·9; H, 8·0. $C_{25}H_{32}O_4$ requires C, 75·7; H, 8·1%), $\nu_{max.}$ (KBr) 2720br (OH) and 1640 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 237, 266, 291, 314, and 380 nm. (log ε 4·45, 4·55, 4·06, 3·64, and 3·74), τ (CCl_4) —2·80 (1H, s, exchangeable, OH), 2·72 (1H, d, J 9 Hz, ArH), 3·12 (1H, s, ArH), 3·44 (1H, d, J 9 Hz, ArH), 6·30 (2H, t, J 7 Hz, $ArO{\cdot}CH_2{\cdot}CH_2$), 7·30 (3H, s, ArMe), 7·67 (3H, s, ArMe), 7·8 (2H, t, J 7 Hz, $ArCH_2{\cdot}CH_2$), 8·0—8·8 (6H, m, 2 × $CH_2{\cdot}CHMe_2$), and 9·0 (12H, d, J 7 Hz, CHMe_2).

Elution with light petroleum (b.p. 40—60°)–ether (85 : 15 v/v) yielded a pale yellow solid (23 mg.; R_F 0·23) which gave the *hydrogenolysis product* of anhydroarugosin (XXIII) as yellow microcrystals, m.p. 134—136° (from n-pentane) [Found: C, 73·9; H, 6·8%; *M* (mass spectrometry), 326. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%; *M*, 326], $\nu_{max.}$ 3440 (OH), 2860 (OH), and 1640 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 238, 268, 293, and 385 nm. (log ε 4·42, 4·51, 4·04, and 3·74), τ ($CDCl_3$) —3·14 (1H, s, exchangeable, OH), 2·56 (1H, d, J 9 Hz, ArH), 2·97 (1H, s, ArH), 3·31 (1H, d, J 9 Hz, ArH), 6·6vbr (1H, s, ArOH), 7·2 (3H, s, ArMe), 7·60 (3H, s, ArMe), 7·74 (2H, t, $ArCH_2{\cdot}CH_2$), 8·0—8·68 (3H, m, $CH_2{\cdot}CHMe_2$), and 9·0 (6H, d, J 7 Hz, CHMe_2).

Hydrogenation of Deisopentenylanhydroarugosin.—Deisopentenylanhydroarugosin (34 mg.) in acetic acid (10 ml.) was shaken at 20° with 10% palladium–carbon (35 mg.) for 12 hr. under hydrogen. The solid obtained (29 mg.) furnished the *dihydro-derivative* (XVII) as yellow needles, m.p. 168—169° (from n-pentane) (Found: C, 70·5; H, 6·0. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%), $\nu_{max.}$ ($CHCl_3$) 2220br (OH) and 1640 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 222, 235, 247, 268, 300, and 410 nm. (log ε 3·32, 4·34, 4·33, 4·24, and 3·68), τ (CCl_4) —3·52 (1H, s, exchangeable, OH), —2·80 (1H, s, exchangeable, OH), —1·48 (1H, s, ArCHO), 2·55 (1H, d, J 9 Hz, ArH), 2·54 (1H, s, ArH), 3·22 (1H, d, J 9 Hz, ArH), 7·70 (3H, s, ArMe), 8·20 (2H, m, $ArCH_2{\cdot}CH_2$), 8·30—8·72 (3H, m, $CH_2{\cdot}CHMe_2$), and 9·0 (6H, d, J 7 Hz, CHMe_2).

Methylation of Deisopentenylanhydroarugosin.—The C_{20} anhydro-derivative (40 mg.) was treated with cold methyl iodide and potassium carbonate in anhydrous acetone for 48 hr. The *di-O-methyldeisopentenylanhydroarugosin* (XVI) was obtained as pale yellow needles (36 mg.), m.p. 100° [Found: *M* (mass spectrometry), 366·1467 ± 0·0016. $C_{22}H_{22}O_5$ requires *M*, 366·1467], $\nu_{max.}$ 1700 (ArCHO) and 1645 (CO) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 212, 245, 275infl, 302infl, and 358 nm. (log ε 4·34, 4·58, 4·12, 3·72, and 3·75), τ (CCl_4) —0·40 (1H, s, ArCHO), 2·64 (1H, d, J 8 Hz, ArH), 2·72 (1H, s, ArH), 3·0 (1H, d, J 8 Hz, ArH), 4·82br (1H, m, $ArCH_2{\cdot}CH{=}$), 6·17 (3H, s, ArOMe), 6·21 (3H, s, ArOMe), 6·68 (2H, d, J 7 Hz, $ArCH_2$), 7·63 (3H, s, ArMe), and 8·27 (6H, s, $Me_2C{=}$).

Treatment of Arugosin with Sodium Borohydride.—Arugosin (1·32 g.) in aqueous methanol was treated with sodium borohydride (250 mg.) at 20° for 6 hr. After removal of the solvent and acidification, the residue was extracted into ether and chromatographed on silica gel (200—300 mesh) with gradient elution. Intermediate fractions eluted with 5% ether–light petroleum (b.p. 40—60°) furnished the *product* (XIX) as a colourless solid (365 mg.), m.p. 127—129° [Found: C, 73·0; H, 7·5%; *M* (mass spectrometry), 410. $C_{25}H_{30}O_5$ requires C, 73·1;

H, 7·4%; *M*, 410], $\nu_{max.}$ 3380 (OH), 3310 (OH), and 3200 (OH) cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 223 and 285 nm. (log ε 4·29 and 3·75), *m/e* 178 ($C_{11}H_{14}O_2$, 74%) and 165 ($C_9H_9O_3$, 67%).

Methylation of the Product (XIX).—Compound (XIX) (85 mg.) was methylated in the usual way to yield the *tri-O-methyl derivative* (XXI) as colourless prisms (from light petroleum) (72 mg.), m.p. 100° [Found: C, 74·2; H, 8·1; OMe, 20·7%; *M* (mass spectrometry), 452. $C_{28}H_{36}O_5$ requires C, 74·3; H, 8·0; 3 × OMe, 20·6%; *M*, 452], $\lambda_{max.}$ (EtOH) 221 and 284 nm. (log ε 4·31 and 3·67), τ (CCl_4) 2·92 (1H, d, *J* 8 Hz, ArH), 3·30br (1H, s, $Ar_2CH{\cdot}O$), 3·40 (1H, s, ArH), 3·44 (1H, d, *J* 8 Hz, ArH), 4·3—4·9 (4H, m, ArC*H*·O and 2 × C=C*H*), 5·62 (2H, d, *J* 7 Hz, $ArO{\cdot}CH_2$), 6·35 (3H, s, ArOMe), 6·45 (6H, s, 2 × ArO*Me*), 6·70 (2H, d, *J* 7 Hz, $ArCH_2{\cdot}CH{=}$), 7·73 (3H, s, ArMe), and 8·27 (12H, s, 2 × $Me_2C{=}$).

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