The Chemistry of the Aristolochia *Species. Part II.* Some Rearrangements of Aristolactone.*

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Aristolactone, $C_{15}H_{20}O_2$, is an αβ-unsaturated γ-lactone containing two other isolated double bonds. Hydrogenation gave first dihydroaristolactone and, finally, the hexahydro-compound. Base-catalysed rearrangement of aristolactone in ethanol and methanol yielded γ-keto-esters. Acid-catalysed isomerisation of aristolactone gave *iso*aristolactone which was converted on hydrogenation first into dihydro- and then into hexahydro-aristolactone.

IN Part I * we described the isolation from the roots of *Aristolochia reticulata* of a crystalline lactone, aristolactone, $C_{15}H_{20}O_2$.

Aristolactone, exhibited a light-absorption maximum at 211 mμ (*c*, 11,500) attributed to an αβ-unsaturated ester or lactone function; failure to isolate an alcohol, and the quantitative recovery of the acidic fraction after hydrolysis supported the assignment of a lactone. A small portion only of the acid crystallised, and this gave a crystalline, but unstable, *S*-benzylthiuronium salt. The bulk of the acid was unstable, rapidly changing into a neutral oil, which could not be characterised. Determination of the iodine value indicated the

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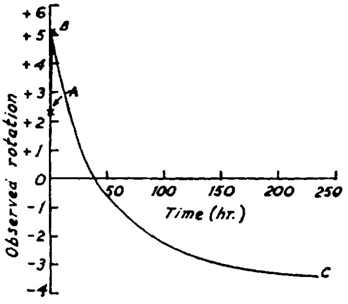
* Part I, *J. Pharm. Pharmacol.*, 1954, **6**, 1005.

equivalent of 2·3 ethylenic bonds in aristolactone, the fractional value being attributed to slow addition of halogen at the double bond associated with the lactone carbonyl group.

The presence of a third double bond was confirmed by microhydrogenation. Hydrogenation on a larger scale was slow and yielded the saturated (tetranitromethane) hexahydroaristolactone, m. p. 103·5—104°. Subsequent hydrogenations, however, yielded mixtures of two different crystalline forms, needles, m. p. 99—100°, and plates, m. p. 100—102°. The chemical identity of these two materials was confirmed by microanalysis, by their infrared spectra, and by hydrolysis to the same hydroxy-acid (see below). The mixed m. p. curve showed a maximum in the range 101—104°. The large negative shift of optical rotation which accompanies the hydrogenation of aristolactone is attributed to the presence of one or more asymmetric centres in close association with a double bond (cf. Chanley and Polgar, *J.*, 1954, 1003).

Hexahydroaristolactone, unlike aristolactone (see below), was stable to cold, but was readily hydrolysed by hot ethanolic potassium hydroxide. The hydroxy-acid, obtained from both crystalline forms of hexahydroaristolactone, was readily reconverted into the parent lactone (needle form) when heated just above its melting point in a sealed tube. Trace amounts of a second, saturated, acid, m. p. 121—122°, were also isolated from the hydrolysis products of hexahydroaristolactone. This acid, however, could not be lactonised, but underwent slow decomposition.

FIG. 1.

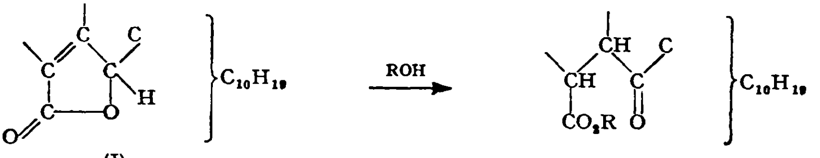


In carbon tetrachloride, aristolactone showed a strong band at 1770 cm.$^{-1}$ (1736 cm.$^{-1}$ in paraffin mull), characteristic of an αβ-unsaturated γ-lactone, with the expected shift to 1780 cm.$^{-1}$ (1750 cm.$^{-1}$ in paraffin mull) in hexahydroaristolactone. Marked changes following hydrogenation are also reflected in the ester-group absorptions in the region 1000—1250 cm.$^{-1}$, the two bands at 1034 and 1064 cm.$^{-1}$ of aristolactone being replaced by a single band at 1167 cm.$^{-1}$ in hexahydroaristolactone. A strong band at 890 and a medium one at 1650 cm.$^{-1}$, which are present in the spectrum of aristolactone (in carbon disulphide) and absent from that of hexahydroaristolactone are attributed to a vinylidene group. This conclusion has been confirmed by the identification of formaldehyde as a product of ozonolysis. Medium bands at 782 and 840, and a weak band at 800 cm.$^{-1}$ present in the spectrum of aristolactone, are likewise absent from that of hexahydroaristolactone, and suggest that of the two remaining double bonds, one at least is tetrasubstituted.

Hydrolysis of aristolactone was accompanied by marked changes of optical rotation, indicative of structural alterations more complex than the opening of the lactone ring. Treatment with cold ethanolic potassium hydroxide caused an initial positive shift up to the maximum which was relatively rapid, being complete within *ca.* 40 min. The succeeding fall was very much slower, a constant negative value being reached only after about 10 days. Titration of a series of aliquot portions, withdrawn during the reaction, showed that, whereas the initial increase of rotation did not involve utilisation of alkali, the succeeding fall in rotation was accompanied by neutralisation of one equivalent. The first reaction is therefore regarded as a base-catalysed rearrangement, and the second reaction as the hydrolysis of the primary product.

The product, isolated in high yield at the point of maximum rotation, was a neutral substance, apparently formed by the addition of the elements of ethanol to aristolactone. Repeated recrystallisation of the product from acetone–water showed that ethanol was not present as solvent of crystallisation. The infrared spectrum (paraffin mull) showed peaks at 1726 and 1186 cm.$^{-1}$ (ester carbonyl); peaks at higher frequencies which could be associated with the original lactone function were absent. The presence of an isolated carbonyl group was established by a low-intensity absorption maximum at 291 mμ (ε, 250), and confirmed by a shoulder at 1704 cm.$^{-1}$.

The formation and properties of this product are characteristic of keto-esters formed by alkaline rearrangement of other αβ-unsaturated lactones (Paist, Blout, Uhle, and Elderfield, *J. Org. Chem.*, 1941, **6**, 273; McKean and Spring, *J.*, 1954, 1989), and establish the partial structures (I and II; R = Et) for aristolactone and this ester, respectively. The loss of a double bond in the formation of the ester, ethyl oxoaristate, was confirmed by microhydrogenation and by determination of iodine value. Hydrogenation gave an oily saturated ester (equivalent, 281), which on hydrolysis yielded an acid also as an oil. This oil showed an absorption maximum at 287 mμ (ε 51), consistent with the carbonyl group's being resistant to hydrogenation under the conditions used.



(I) (II)

Treatment of aristolactone with methanolic potassium hydroxide similarly gave methyl oxoaristate. Since this ester could be isolated pure more readily than the ethyl ester it was used in preference to the latter in all our later experiments. The absorption spectrum of methyl oxoaristate in carbon disulphide showed peaks at 1735 and 1150—1200 (broad band; carboxylic ester) and at 1720 cm.$^{-1}$ (ketone). Peaks at 890 and 1650 cm.$^{-1}$ (vinylidene) were identical in position and intensity with those of the parent lactone, indicating that the vinylidene group was apparently unaffected by the alkaline rearrangement. Peaks at 782, 800, and 840 cm.$^{-1}$ observed in the spectrum of aristolactone were also present in that of methyl oxoaristate, though much reduced in intensity. This demonstrates the tetrasubstitution of the second double bond of methyl oxoaristate and suggests that the third double bond, which is eliminated in the alkaline rearrangement of aristolactone, may possibly also be tetrasubstituted. These conclusions are supported by the ultraviolet absorption spectra, which showed a small shift in the maximum and a reduction in its intensity from 211 mμ (ε, 11,500) in aristolactone to 209 mμ (ε, 6360) in methyl oxoaristate and 209 mμ (ε, 7000) in ethyl oxoaristate. The position and intensity of the maxima for methyl and ethyl oxoaristate are characteristic of a tetrasubstituted ethylenic bond (Halsall, *Chem. and Ind.*, 1951, 867).

Further evidence for the rearrangement postulated comes from the observation that the bands in the spectrum of hexahydroaristolactone at 953 and 1010 cm.$^{-1}$, attributed to a *cyclo*hexane ring (Marrison, *J.*, 1951, 1614), were replaced in the spectrum of methyl oxoaristate by one at 1100 cm.$^{-1}$ (*cyclo*hexanone derivatives; cf. Lécompte, *Compt. rend.*, 1945, **221**, 50). These bands also provide evidence for the presence of a second ring in aristolactone, and support the thesis (based upon its formulation as $C_{15}H_{20}O_2$ with three double bonds) that the parent lactone is bicyclic, so that the second ring can be tentatively assigned as six-membered.

Ethyl oxoaristate was first obtained by the catalysed reaction of ethanolic ammonia on the lactone. Ammonia is known to form adducts with certain αβ-unsaturated lactones (Hansen, *Ber.*, 1931, **64**, 67; Ruzicka and Pieth, *Helv. Chim. Acta*, 1931, **14**, 1090), and although aristolactone failed to form such an adduct, a catalysed reaction with ethanolic ammonia in the presence of traces of zinc dust gave ethyl oxoaristate. The reaction, which was followed polarimetrically, was complete in *ca.* 72 hours, the rotation having then reached a maximum. If permitted, this reaction also continued with the same slow fall of rotation observed when ethanolic potassium hydroxide had been used. Methanolic ammonia, in the presence of zinc dust, reacted much more rapidly to give methyl oxoaristate.

Aristolactone was isomerised by boiling glacial acetic acid to a new lactone, *iso*aristolactone. Much resinification occurred and some material was recovered as an oil of similar rotation to that of *iso*aristolactone, but which was unchanged by further treatment with glacial acetic acid. The ultraviolet absorption spectrum of *iso*aristolactone was similar to that of aristolactone but also showed a low-intensity maximum at 272 mμ (ε, 640).

*iso*Aristolactone was non-aromatic (yellow colour with tetranitromethane), and was hydrolysed only very slowly by boiling ethanolic potassium hydroxide. The seat of the isomerisation is therefore in or near the lactone ring, and *iso*aristolactone cannot be represented as an αβ-unsaturated lactone, with an endocyclic double bond as in (I). Complete hydrogenation of *iso*aristolactone confirmed the presence of three ethylenic bonds and gave hexahydroaristolactone as sole product, indicating that the isomerisation was not a stereoisomeric change. The hydrogenation showed a definite break in rate of hydrogen uptake after the rapid absorption of 1 mol., and then gave a dihydro-compound in excellent yield. This difference from aristolactone, which showed a break in uptake after the slow absorption of 2 mols., supported the hypothesis that a double-bond shift had occurred in the isomerisation. This was confirmed by the isolation of dihydroaristolactone (identical with the dihydro-compound from *iso*aristolactone) from the controlled hydrogenation of aristolactone.

Spectroscopic evidence supports the view that the same double bond is involved in both acid and alkaline rearrangements. In carbon disulphide *iso*aristolactone showed typical vinylidene bands at 892 (s) and 1655 cm.$^{-1}$ (m) of the same intensity as those in the parent lactone. Bands at 787 (m) and 842 cm.$^{-1}$ (m) (tetrasubstituted ethylene), however, were of similar intensity to those recorded for methyl oxoaristate (reduced intensity compared with aristolactone). Dihydroaristolactone showed similar bands, and, moreover, exhibited a maximum at 209 mμ (ε, 7800) (isolated tetrasubstituted ethylene). Further evidence for the double-bond shift is adduced from comparison of the ultraviolet absorption spectra of aristolactone and *iso*aristolactone (Fig. 2). The broader maximum shown by aristolactone at 211 mμ is in accord with that expected for the summation of the band due to the isolated tetrasubstituted ethylene at 209 mμ with that at a longer wavelength due to the αβ-unsaturated lactone function (cf. Barton and de Mayo, *J.*, 1954, 887). The much more sharply defined maximum at 209 mμ in *iso*aristolactone in which the carbonyl group is not αβ-unsaturated, is regarded as the summation of two similar peaks, both at the same wavelength, one being due to the isolated tetrasubstituted double bond as in dihydroaristolactone. Comparison of the molecular extinction coefficients of dihydroaristolactone and *iso*aristolactone suggests that the new double bond in *iso*aristolactone may be trisubstituted.

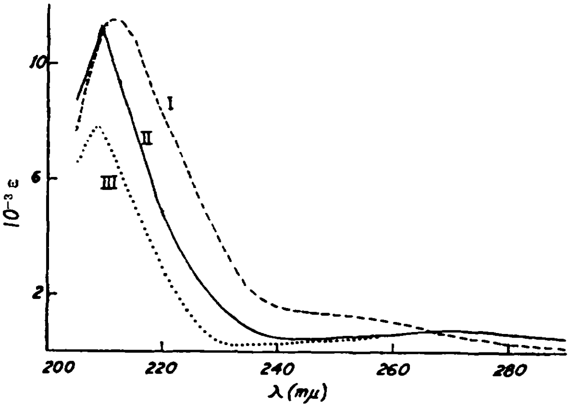


FIG. 2.
I, Aristolactone.
II, *iso*Aristolactone.
III, Dihydroaristolactone.

EXPERIMENTAL

M. p.s are uncorrected. Rotations were determined in absolute ethanol (unless otherwise stated) in a 1-dm. tube. Ultraviolet absorption spectra were determined in absolute ethanol on a Hilger Uvispek photoelectric spectrophotometer; infrared absorption spectra by using a recording double-beam infrared spectrometer, built in this College by Dr. I. A. Brownlee (*J. Sci. Instr.*, 1950, **27**, 215). We are indebted to Mr. A. Pajaczkowski and Dr. G. Houghton for these measurements and to Mr. W. McCorkindale and Dr. A. C. Syme for the micro-analyses.

Aristolactone.—This was isolated from the petrol-soluble extract of *Aristolochia reticulata* as described in Part I and formed needles (from acetone–water), m. p. 110·5—111°, $[\alpha]_D^{14}$ +156·4° (*c*, 1), $\lambda_{max.}$ 211 mμ (ε, 11,500) [Found: C, 77·5; H, 8·8%; equiv. (by hydrolysis), 233; *M* (Rast), 227 ± 13. Calc. for $C_{15}H_{20}O_2$: C, 77·6; H, 8·7%; equiv., 232; *M*, 232). Infrared spectrum: (*a*) 0·5M in carbon tetrachloride—peaks at 1770 (αβ-unsaturated γ-lactone), 1034, and 1060 (ester function); (*b*) in paraffin mull—peak at 1736 (αβ-unsaturated γ-lactone); (*c*) 0·5M in carbon disulphide—peaks at 1650 (m) and 890 (s) (vinylidene), 840 (m), 800 (w), and 782 (m) cm.$^{-1}$ (tetrasubstituted ethylene). The iodine value (determined by the method of the British Pharmacopœia) was equivalent to 2·3 double bonds.

Hydrolysis. (*a*) Aristolactone (216 mg.) was refluxed for 30 min. with ethanolic potassium hydroxide (0·66N; 3 ml.), and the solution, after acidification, extracted with ether to yield a viscous oil (207 mg.). This partly crystallised to an acid, m. p. 118°. The residual oil (140 mg.; equiv., 363), after neutralisation with 0·1N-sodium hydroxide and extraction with light petroleum, yielded a neutral oil (52 mg.); acidification of the aqueous solution and extraction with ether gave an acidic oil (87 mg.) similar to that described above.

(*b*) Aristolactone (72·8 mg.) was dissolved in cold ethanolic potassium hydroxide (0·66N; 5 ml.) and the solution examined polarimetrically (1 dm. tube; 13°). The rotations observed are plotted in Fig. 1.

(*c*) Aristolactone (261 mg.) was dissolved in ethanol (90%) which had been freed from carbon dioxide, freshly prepared N-ethanolic potassium hydroxide (3 ml.) was added, and the solution made up to 50 ml. with ethanol (90%). At intervals aliquot parts (5 ml.) were titrated with 0·05N-hydrochloric acid, the rotation of the alkaline solution being determined at the same time. The results are shown in the Table.

Neutralisation of fractions 7 and 8 yielded ethyl oxoaristate, m. p. 55° (see below). The product isolated from fraction 10 was an oily acid, which failed to crystallise.

Time (min.) ...	0	5	10	15	25	35	55	75	30 (days)	38 (days)
$[\alpha]_D^{18}$	+1·05°	+1·38°	+1·53°	+1·65°	+1·74°	+1·78°	+1·81°	+1·79°	−0·30°	−0·48°
0·05N-KOH neutralised (ml.)	0·00	0·02	—	0·13	0·23	0·22	0·31	0·31	2·22	2·34

Hexahydroaristolactone.—Aristolactone (1·3 g.) was hydrogenated in ethanol in presence of platinum; 3·0 mols. of hydrogen were absorbed. Evaporation of the solvent gave *hexahydroaristolactone* in feathery needles, m. p. 103·5—104°, $[\alpha]_D^{17}$ +3° (*c*, 1·2%), from light petroleum [Found: C, 75·65; H, 11·1%; equiv. (by hydrolysis), 233. $C_{15}H_{26}O_2$ requires C, 75·6; H, 11·0%; equiv., 238]. Infrared spectrum: (*a*) 0·5M in carbon tetrachloride—peaks at 1780 (saturated γ-lactone), 1167 (ester function); (*b*) in paraffin mull—1750 (saturated γ-lactone). Subsequent hydrogenations yielded hexahydroaristolactone first in needles, m. p. 99—100°, and then in plates, m. p. 100—102°, $[\alpha]_D^{17}$ +3° (Found: C, 75·2; H, 11·4%). The infrared spectra were identical with that described above. A mixture of the needles and the plates had m. p. 101—104°.

Dihydroaristolactone.—Aristolactone (276 mg.) was hydrogenated in ethanol in presence of palladium–charcoal, the reaction being stopped after the absorption of 1 mol. of hydrogen. Evaporation of the solvent gave dihydroaristolactone, m. p. 79—80·5°, $[\alpha]_D^{17}$ −77° (from light petroleum).

Hydrolysis of Hexahydroaristolactone.—(*a*) Hexahydroaristolactone (needles; m. p. 103·5—104°; 121 mg.) was refluxed with ethanolic potassium hydroxide (0·66N; 5 ml.) for 30 min., and the solution acidified and extracted with light petroleum to yield plates, m. p. 86—87° (from light petroleum), $[\alpha]_D^{16}$ +16° (*c*, 1·6) (Found: C, 70·3; H, 11·2. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0%). Fractional crystallisation of the mother liquors yielded a small quantity of a second acid, in short needles, m. p. 121—122°, insufficient for characterisation. The acid did not give a yellow colour with tetranitromethane.

(*b*) Hexahydroaristolactone (plates; m. p. 100—102°; 300 mg.) was refluxed with ethanolic potassium hydroxide (0·66N; 5 ml.) for 30 min. The *product* (Found: equiv., 239. $C_{15}H_{28}O_3$ requires equiv. 238) isolated as in (*a*), formed plates, m. p. 86—87° undepressed on admixture with the acid obtained from (*a*).

The acid (m. p. 86—87°; 32 mg.) was heated in a sealed tube at 100° for 3 hr. over phosphoric oxide. After sublimation, hexahydroaristolactone was isolated as feathery needles, m. p. and mixed m. p. 100—103°.

Ethyl Oxoaristate.—Aristolactone (156·5 mg.) was dissolved in a mixture of N-ethanolic potassium hydroxide (2 ml.) and ethanol (90%; 25 ml.); the solution was neutralised with

0·1N-hydrochloric acid as soon as the optical rotation reached a maximum. Dilution with water yielded *ethyl oxoaristate* (126 mg.) in needles, m. p. 56—57° (from acetone–water), $[\alpha]_D^{19}$ +317° (*c*, 1), $\lambda_{max.}$ 209 mμ (ε, 7000) and 291 mμ (ε, 250) (Found: C, 73·1; H, 9·4. $C_{17}H_{26}O_3$ requires C, 73·3; H, 9·3%). Infrared spectrum in paraffin mull: peaks at 1726 and 1186 (ester carbonyl); 1704 (sh) cm.$^{-1}$ (ketone). Iodine value equivalent to 2·5 double bonds.

Hydrogenation of Ethyl Oxoaristate.—(*a*) Ethyl oxoaristate (3·2 mg.) when hydrogenated in acetic acid in the presence of platinum absorbed 1·95 mols. of hydrogen.

(*b*) Ethyl oxoaristate (117 mg.) was hydrogenated in ethanol in presence of platinum. Evaporation of the solvent gave an almost colourless oil (115 mg.) (probably *ethyl tetrahydro-oxoaristate*) [Found: equiv. (by hydrolysis), 281. $C_{17}H_{30}O_3$ requires equiv., 282]. Acidification of the hydrolysis liquors and extraction with light petroleum gave an acidic oil (75 mg.), $\lambda_{max.}$ 287 (ε, 51), which only partially crystallised after several weeks.

Methyl Oxoaristate.—Aristolactone (252 mg.) was dissolved in N-methanolic potassium hydroxide (2 ml.) and methanol (90%; 25 ml.); .the product, isolated as above, yielded *methyl oxoaristate* (250 mg.) in needles, m. p. 68—69° (from aqueous ethanol), $[\alpha]_D^{14}$ +342° (*c*, 1·23), $\lambda_{max.}$ at 209 mμ (ε, 6360) and 290 mμ (ε, 264) (Found: C, 72·1; H, 9·1. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·1%). Infrared spectrum: peaks at 1650 (m) and 890 (s) (vinylidene), 840 (w), 800 (w), and 781 (w) (tetrasubstituted ethylene), 1735 and 1150—1200 (broad band) (ester carbonyl), 1720 (ketone), and 1100 cm.$^{-1}$ (*cyclo*hexanone derivative). Iodine value equivalent to 2·15 double bonds.

Hydrolysis. Methyl oxoaristate (162 mg.) was refluxed with ethanolic potassium hydroxide (0·66N; 5 ml.) (Found: equiv., 266. $C_{16}H_{24}O_3$ requires equiv., 264). The hydrolysis liquors were acidified, saturated with sodium chloride, and extracted with light petroleum yielding an extremely viscous oil (178 mg.).

Reactions of Aristolactone with Alcoholic Ammonia.—(*a*) Arisolactone (50 mg.) was dissolved in ethanol (95%; 5 ml.), and the solution was saturated with ammonia and set aside overnight. Concentration and dilution with water gave unchanged aristolactone, m. p. 107—109°.

(*b*) Aristolactone (74 mg.) was dissolved in ethanol (95%; 5 ml.), zinc dust (30 mg.) added, and the solution saturated with ammonia. The product isolated at the point of maximum optical rotation (after 3 days) was separated by concentration and dilution with water. Crystallisation from ethanol (70%) yielded needles of ethyl oxoaristate (35 mg.), m. p. 56—57° (Found: C, 73·8; H, 9·5. Calc. for $C_{17}H_{26}O_3$: C, 73·3; H, 9·3%).

(*c*) Aristolactone (30 mg.), when treated with *iso*propanol, ammonia, and zinc dust as in (*b*), was recovered unchanged.

(*d*) Aristolactone (70 mg.) when treated with methanolic ammonia in the presence of zinc dust as in (*b*) yielded methyl oxoaristate (26 mg.), m. p. 68—69° (from 70% *ethanol*), undepressed on admixture with a sample prepared from aristolactone and methanolic potassium hydroxide.

(*e*) Aristolactone (30 mg.), after treatment with triethylamine (0·5 ml.) in ethanol in the presence of zinc dust as in (*b*), was obtained unchanged.

iso*Aristolactone.*—Aristolactone (1 g.) in acetic acid (10 ml.) was heated for 12 hr. in an atmosphere of carbon dioxide at 130°. Removal of the solvent under reduced pressure gave a brown oil, which was dissolved in light petroleum, filtered from resinous material (0·1 g.), and washed with aqueous sodium hydrogen carbonate and then with water. Concentration and crystallisation gave iso*aristolactone* (0·15 g.), m. p. 90—91°, $[\alpha]_D^{17}$ −44° (*c*, 1·4), $\lambda_{max.}$ 209 mμ (ε, 11,200) and 272 mμ (ε, 640) (Found: C, 77·55; H, 8·7. $C_{15}H_{20}O_2$ requires C, 77·6; H, (8·6%). Infrared spectrum in carbon disulphide (0·5M): peaks at 892 (s) and 1655 (vinylidene) and 787 (m) and 842 cm.$^{-1}$ (m) (tetrasubstituted ethylene). Iodine value equivalent to 2·35 double bonds. A second crop of crystals (0·2 g.; m. p. 83—87°) and an oil (0·48 g.; $[\alpha]_D^{17}$ −38·1°) were also obtained. The latter was unchanged on further treatment with boiling acetic acid.

*Attempted hydrolysis. iso*Aristolactone (106 mg.) was refluxed with ethanolic potassium hydroxide (0·66N; 2 ml.) for 40 min. The solution was diluted and neutralised with 0·05N-sulphuric acid, giving *iso*aristolactone (46 mg.), m. p. and mixed m. p. 90—91°. The mother liquors were extracted with light petroleum, acidified, then re-extracted with light petroleum, and dried (Na_2SO_4), yielding an acidic oil.

Hydrogenation. (*a*) *iso*Aristolactone (140 mg.), when hydrogenated in ethanol in presence of platinum for 48 hr., absorbed 3·2 mols. of hydrogen, and yielded needles of hexahydroaristolactone, m. p. and mixed m. p. 102—104° [Found: equiv. (by hydrolysis), 242. Calc. for $C_{15}H_{26}O_2$: equiv., 238].

(*b*) *iso*Aristolactone (111 mg.) was hydrogenated for 10 min. in ethanol in presence of platinum; 0·9 mol. of hydrogen was absorbed. Evaporation of the solvent gave needles of *dihydroaristolactone*, m. p. 79·5—80°, $[\alpha]^{17}$ −75°, $\lambda_{max.}$ 209 mμ (ε, 7800) and 271 mμ (ε, 606) (Found: C, 77·0; H, 9·5. $C_{15}H_{22}O_2$ requires C, 76·85; H, 9·5%). Infrared spectrum in carbon disulphide (0·5M): peaks at 894 (ms) and 1673 (w) (vinylidene?), 1775 (s) (saturated γ-lactone), and 782 (m) and 840 (m) cm.$^{-1}$ (tetrasubstituted ethylene). A mixture with authentic dihydroaristolactone had m. p. 78—80°.

Ozonolysis of Aristolactone.—Aristolactone (0·5 g.) was ozonised at −30° in ethyl acetate for 30 min., and the product subsequently hydrogenated in the presence of platinum in the same solvent. Water-soluble products were extracted by being shaken with saturated aqueous sodium chloride. The water-insoluble fraction was concentrated and yielded a water-immiscible oil, which gave a positive reaction with Schiff's reagent and yielded an amorphous mixture of 2 : 4-dinitrophenylhydrazones. The aqueous distillate from the brine solution gave a positive Schiff's reaction for aldehydes, but no reaction for ketones. Formaldehyde was identified by oxidation with hydrogen peroxide to formic acid, the solution then giving a negative Schiff's reaction, but readily reducing mercuric chloride. Formaldehyde was confirmed by conversion into the dimedone derivative, m. p. and mixed m. p. 187—189°.

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