Tetrahedron, 1958, Vol. 4, pp 68–86. Pergamon Press Ltd., London

VOLATILE CONSTITUENTS OF BLACK-ROTTED SWEET POTATO AND RELATED SUBSTANCES

TAKASHI KUBOTA
Institute of Polytechnics, Osaka City University, Minamiogimachi, Kitaku, Osaka, Japan

(*Received* 4 *February* 1958)

Abstract—From the volatile component of sweet potatoes infected by *Ceratostomella fimbriata* ("black rotted" disease), four β-substituted furans, viz. ipomeamarone (1), batatic acid (45), ipomeanine (47) and β-furan carboxylic acid were isolated. The chemical constitutions of the former three compounds were determined by degradations and by synthesis. The chemical constitution of β-substituted furans, viz. ngaione (52) and myoporon (53), which were isolated from essential oil of *Myoporum* plants were determined and the relation of ipomeamarone, ngaione and myoporone was established.

INFECTION of sweet potatoes, *Ipomoea batatas*, by Ascomycetes, *Ceratostomella fimbriata*, causes the so called "black rot disease" and dark brown spots appear on the potatoes. The affected parts have a specific odour and a very bitter taste. The bitter principle is toxic to animals,[1] acts as an antibiotic towards micro-organisms[2] and has an ascaricidal action.[3] The question of how such a substance is formed inside the potato is of considerable interest in plant physiology[4] and enzyme chemistry.

Hiura[5] was the first to make a chemical study of the bitter principle. He identified it and named it ipomeamarone, and showed it to be an unsaturated ketone. Similar results were reported later by Ohno and Takeuchi[6] and Watanabe and Iwata.[3]

The results of the investigation of the volatile toxic products of black-rotted sweet potatoes are now described, and it has been shown that these volatile components are closely related in chemical structure to the components of the essential oil from *Myoporum* species.

Isolation of volatile components of black-rotted sweet potato

The affected part (120 kg) was cut out, finely sliced and extracted with ether, the extract yielding 1·3 kg of crude oil, which was shaken with sodium hydrogen carbonate solution and separated into crude neutral oil (1·2 kg) and sodium hydrogen carbonate solution containing acidic products. The crude neutral oil was repeatedly fractionated under reduced pressure (10^{-2} to 10^{-3} mm) and afforded fractions having the following data:[7]

Fraction	b.p. (10^{-3} mm)	n_D^{22}	$[\alpha]_D$	Yield (g)
Ipomeanine	69–95°	1·490–1·485	+10°	49
Ipomeamarone	100–103°	1·481–1·478	+22–28°	196

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[1] S. Abo and S. Nomura, *J. Verter. Hyg. Ass.* **10**, 17 (1942); S. Nomura and H. Yonemura, *Verter. Sci.* **1**, 5 (1944).

[2] S. Yamashita, *J. Soc. Brewing, Japan* **9**, 88 (1946); I. Yamamoto, S. Suzuki and K. Muramatsu, *Agric. & Hort.* **22**, 515 (1947).

[3] H. Watanabe and H. Iwata, *J. Agric. Chem. Soc. Japan* **23**, 521 (1950).

[4] I. Uritani *et al.*, *J. Agric. Chem. Soc. Japan* **26**, 289 (1953); *Ibid.* **27**, 24, 29, 57, 161, 165, 168, 688, 781, 785, 789 (1954); *Ibid.* **29**, 148, 151, 156, 344, 377, 381 (1955); *J. Biol. Chem. Japan* **41**, 631 (1954); *Ibid.* **43**, 579, 589, 597 (1956).

[5] K. Oze and M. Hiura, *Ann. Rep. Japanese Plant Pathol.* **9**, 123; M. Hiura, *Nogaku*, **7**, 5 (1947); M. Hiura, *Sci. Rep. Gifu Agric. College* No. 50 (1943).

[6] T. Ohno and T. Takeuchi, *Sci. Insect Control* **12**, 26 (1946).

[7] T. Kubota, H. Yamaguchi, K. Naya and T. Matsuura, *J. Chem. Soc. Japan* **73**, 897 (1952).

The ipomeanine portion deposited on standing a small amount of palmitic acid[8]. The sodium hydrogen carbonate solution was extracted with ether to remove the neutral substances completely, acidified with dilute sulphuric acid, and extracted again with ether. The crude acidic oil obtained on evaporation of ether was repeatedly fractionated under a reduced pressure to yield β-furancarboxylic acid (1·0 g) as the sublimate. A fraction of b.p. 90–115° gave crystals of *trans*-cinnamic acid (0·5 g) and the fraction b.p. 115–120° gave crystalline batatic acid (0·8 g).[9] It seemed certain that at least one kind of oily acid with a furan ring is present in this portion, but it has not yet been isolated in a pure state.[10] Valeric and butyric acids in the crude acidic oil were identified by paper chromatography.[9] In this connection, the results of tests for the presence of a furan compound in healthy potatoes were negative.[11]

Structure of ipomeamarone

As stated above, the chief portion is the ipomeamarone fraction, which was repeatedly fractionated, and this fraction was obtained in almost pure state. As shown in Table 1, its physical constants agreed approximately with the data reported by Hiura and Ohno and Takeuchi.

TABLE 1. DATA FOR IPOMEAMARONE FRACTION

Worker	b.p. (°C/mm Hg)	Refractive index	Density	Optical rotation	Semicarbazone m.p. (°C)
Hiura[5]	129°/2·5	—	—	—	131–132
Ohno and Takeuchi[6]	140·4°/6	n_D^{12} 1·4850	d_4^{12} 1·0174	$[\alpha]_D^{12}$ +14·07° (in C_6H_6)	131–132
Writer's	103°/10^{-3}	n_D^{15} 1·4827	d_4^{16} 1·0423	$[\alpha]_D^{25}$ +28·07° (in C_2H_5OH)	133–134

The molecular formula of ipomeamarone (1) agrees with $C_{15}H_{22}O_3$ and it gives a monosemicarbazone of m.p. 133–134°. Since it is negative to Fehling's reagent and fuchsin decolorised with sulphurous acid, it is assumed to possess one ketone group. It does not react with acetic, benzoic or *p*-nitrobenzoic anhydrides, and so the remaining two oxygens must be neutral. Titration of ipomeamarone with bromine in carbon tetrachloride results in the consumption of two molecules of bromine and liberation of two molecules of hydrogen bromide. Titration with perbenzoic acid gives the value of 1·45 and hydrogenation results in the consumption of two molecules of hydrogen. Ipomeamarone forms a maleic anhydride adduct from which the presence of one conjugated double bond may be predicted. Determination of C-methyl group by the Kuhn–Roth method gives a value of 1·85. Oxidation of ipomeamarone with potassium permanganate yields *iso*valeric acid. Based on these observations formula (2) is suggested for ipomeamarone.[12]

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[8] T. Kubota and N. Ichikawa, Unpublished work.

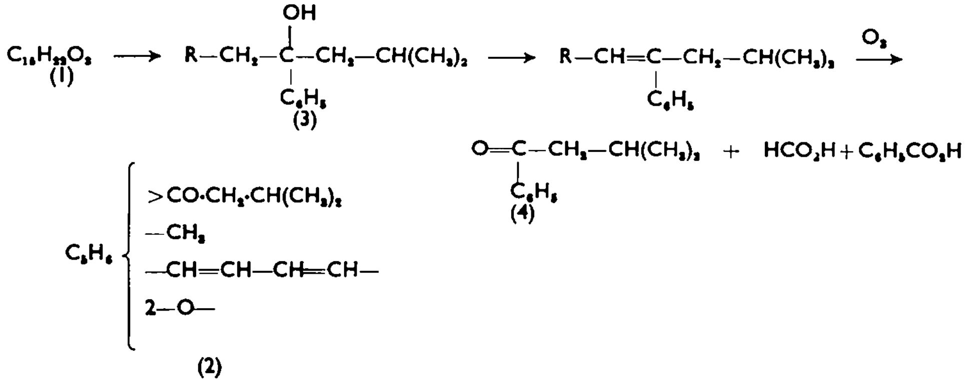
[9] T. Kubota and K. Naya, *J. Chem. Soc. Japan*, 77, 86 (1956).

[10] T. Kubota and K. Naya, Unpublished work.

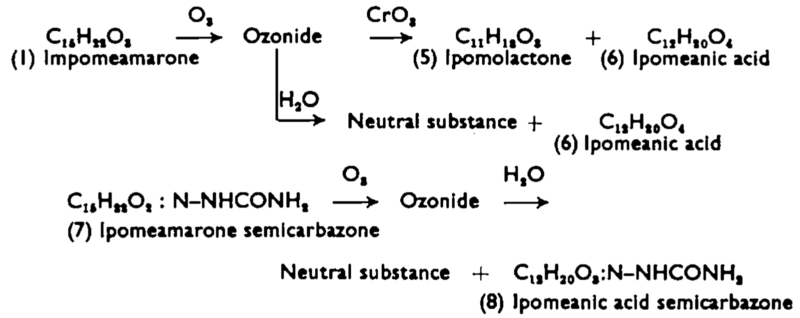
[11] T. Kubota and H. Sakamoto, Unpublished work.

[12] T. Kubota, H. Yamaguchi, K. Naya and T. Matsuura, *J. Chem. Soc. Japan* 74, 44 (1953).

The action of phenylmagnesium bromide on ipomeamarone (1) and dehydration of the carbinol (3) followed by ozonolysis yields *iso*butyl phenyl ketone (4) and the position of the ketone group is known to be bonded to the *iso*butyl group.[13,14]



Ozonolysis of ipomeamarone and oxidative decomposition of the ozonide with chromic acid gives ipomolactone (5), $C_{11}H_{18}O_3$, b.p. 108–112°/10^{-3} mm, $n_D^{9.5}$ 1·4610, and ipomeanic acid (6), $C_{12}H_{20}O_4$, b.p. 108–110°/10^{-3} mm, $n_D^{10.0}$ 1·4533. Decomposition of the ozonide with water gives an unknown neutral substance, ipomeanic acid, formic acid and carbon dioxide, but no crystalline derivatives. Ozonolysis of ipomeamarone semicarbazone (7) and decomposition with water gives ipomeanic acid semicarbazone (8) as crystals of m.p. 166–167°, which agreed with the substance obtained by the reaction of ipomeanic acid (6) and semicarbazide hydrochloride.[15]



In order to determine the structure of ipomolactone (5), the following experiments were carried out.[16] Ring cleavage of the lactone, esterification and distillation effect dehydration and afford methyl anhydroipomate.[9] Ozonolysis of its semicarbazone (10) gives methyl levulinate (11) and disemicarbazone (12) of *iso*butylglyoxal. (12) was identified with the product synthesised from *iso*valerylacetic acid (13). On the other hand, catalytic reduction of (9) and saponification of the semicarbazone of the product affords dihydroanhydroipomic acid semicarbazone (14), m.p. 141–142°.

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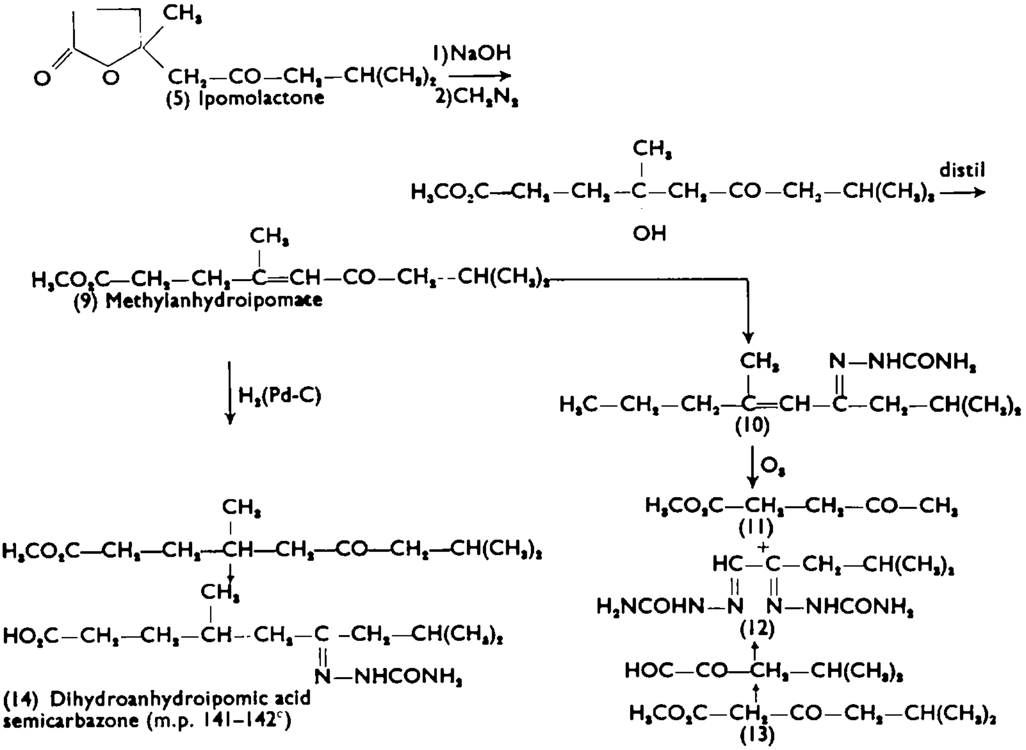
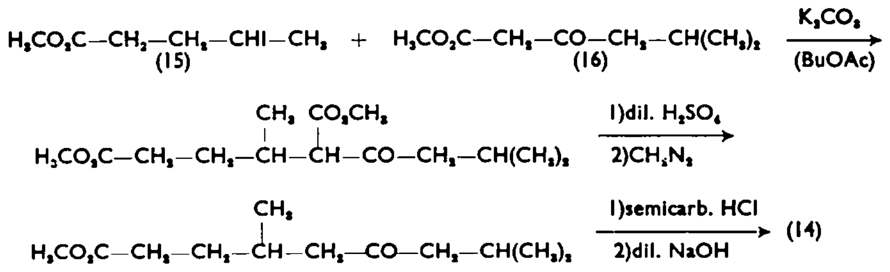
[13] T. Ohno and M. Toyao, *Ann. Meet. Agr. Chem. Japan* (1949).
[14] T. Kubota and T. Matsuura, *J. Chem. Soc. Japan* 73, 530 (1952).
[15] T. Kubota and T. Matsuura, *J. Chem. Soc. Japan* 74, 101 (1953).
[16] T. Kubota and T. Matsuura, *J. Chem. Soc. Japan* 74, 105 (1953).



In order to identify the dihydroanhydroipomic acid semicarbazone as (14), it was synthesised from methyl γ-iodovalerate (15) and methyl *iso*valerylacetate (16).[16]



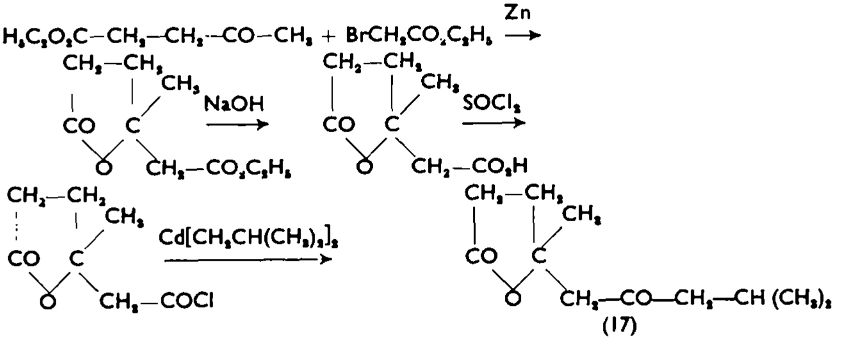
$$\underset{(15)}{H_3CO_2C-CH_2-CH_2-CHI-CH_3} + \underset{(16)}{H_3CO_2C-CH_2-CO-CH_2-CH(CH_3)_2} \xrightarrow[(BuOAc)]{K_2CO_3}$$

$$H_3CO_2C-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CO_2CH_3}{|}}{C}H-CO-CH_2-CH(CH_3)_2 \xrightarrow[2)CH_2N_2]{1)dil.\ H_2SO_4}$$

$$H_3CO_2C-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CO-CH_2-CH(CH_3)_2 \xrightarrow[2)dil.\ NaOH]{1)semicarb.\ HCl} (14)$$

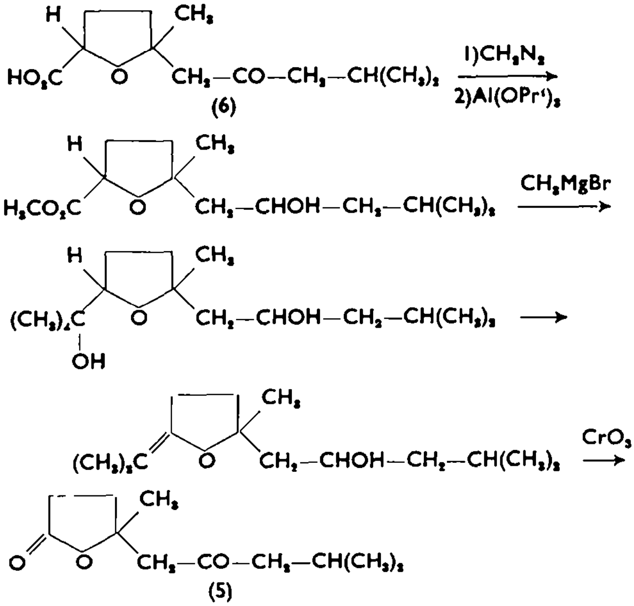
From these results, formula (5) was assumed for ipomolactone and this was confirmed by the synthesis of (±)-ipomolactone.[17] Since ipomolactone does not form any crystalline derivative, the synthetic lactone was converted to dihydroanhydroipomic acid semicarbazone (m.p. 141–142°), which was identified with the same compound from the natural substance.

[17] T. Matsuura, *J. Chem. Soc. Japan* **74**, 668 (1953).



(17)

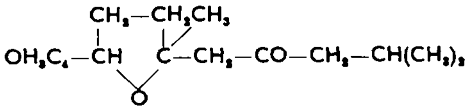
The other fragment obtained on ozonolysis of ipomeamarone, ipomeanic acid (6), $C_{12}H_{20}O_4$, has CH_2O more than ipomolactone (5), $C_{11}H_{18}O_3$. If the structure of ipomolactone is to be represented by (5), ipomeanic acid is assumed to have =CHCOOH in place of =CO in the lactone. This was proved[18] by the fact that one Wieland-Barbier decomposition of ipomeanic acid converts it to the ipomolactone.



(6)

(5)

From the foregoing results, the partial structure of ipomeamarone would be represented by the formula (18) and the doubtful portion is C_4H_3O, which contains a conjugated double bond and one neutral oxygen.



(18)

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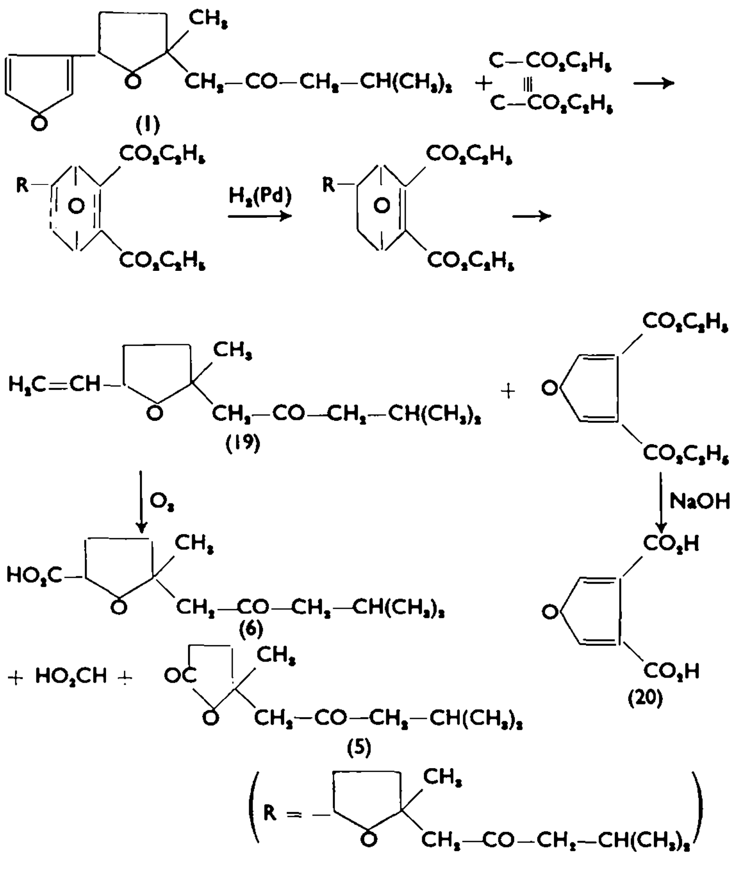
[18] T. Kubota and T. Matsuura, *J. Chem. Soc. Japan* **74**, 197 (1953).

As previously stated, ipomeamarone is coloured crimson with hydrochloric acid, violet red with *p*-dimethylaminobenzaldehyde[19] and blood red with antimony trichloride,[19] so that this doubtful portion would appear to be a furan ring.

In order to prove this structure and to determine the substituted positions on the furan ring, an Alder–Rickert degradation reaction[20] of ipomeamarone was carried out. This reaction resulted in the formation of furan-3:4-dicarboxylic acid (20), together with a neutral unsaturated ketone (19), indicating this portion to be a *β*-substituted furan ring. This has established the structure of ipomeamarone to be formula (1).[21]



Synthesis of ipomeamarone

When the natural (+)-ipomeamarone (1) is boiled with acetic anhydride and potassium acetate for a long time,[22] the tetrahydrofuran ring is cleaved to form (±)-acetyl*iso*ipomeamarone (21),[23,24] accompanied by racemisation. Saponification

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[19] T. Reichstein, *Helv. Chim. Acta* **15**, 1110 (1932); P. Karrer and H. Schmidt, *Ibid.* **29**, 525 (1946).

[20] K. Alder and H. F. Rickert, *Ber. Dtsch. Chem. Ges.* **70**, 1354 (1934).

[21] T. Kubota and T. Matsuura, *J. Chem. Soc. Japan* **74**, 248 (1953).

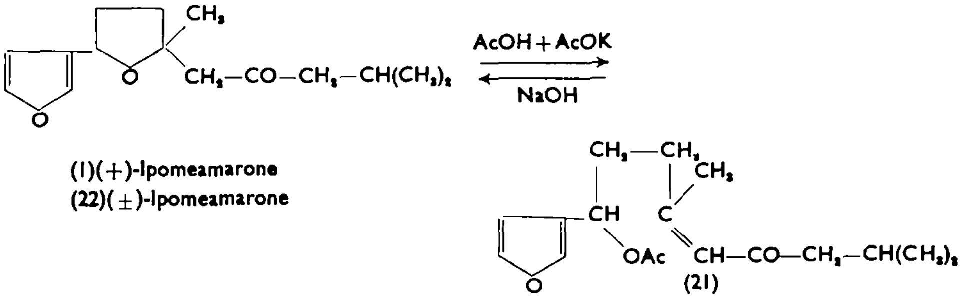
[22] A. J. Birch, R. Massy-Westropp and S. E. Wright *Austr. J. Chem.* **6**, 385 (1953).

[23] T. Kubota and T. Matsuura, *J. Chem. Soc. Japan* **78**, 386 (1956).

[24] A. J. Birch, R. Massy-Westropp, S. E. Wright, T. Kubota and T. Matsuura, *Chem. & Ind.* 902 (1954).

of (21) with alkali causes it to revert to (±)-ipomeamarone (22). Since this reaction indicates that there is no change in the steric configuration of αα′-position in the tetrahydrofuran ring, it would seem possible to synthesise ipomeamarone via the compound of type (21).

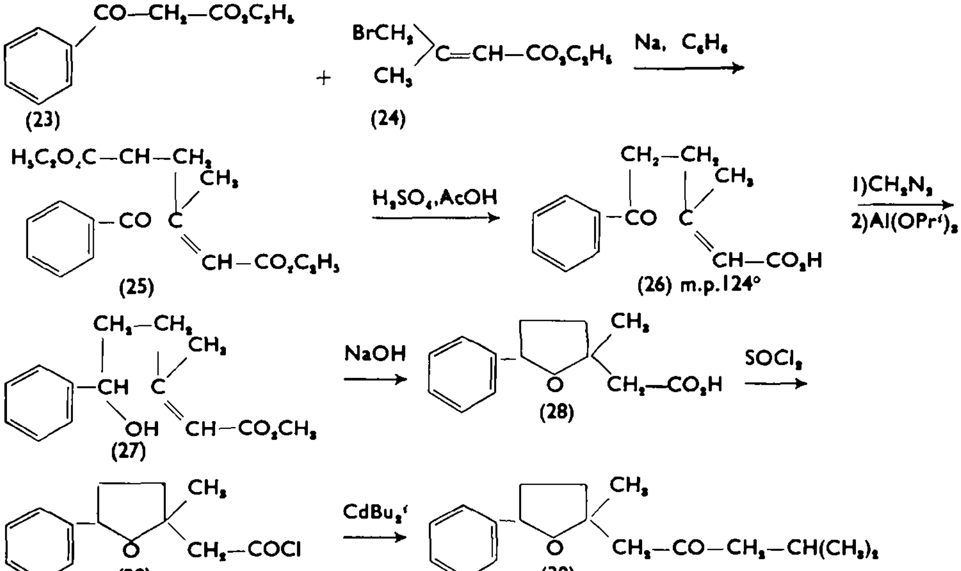
An attempt was first made to synthesise the compound (30) having a benzene ring in place of the furan ring and an oil of b.p. 110°/10^{-3} mm, n_D^{22} 1·5006, was



(1)(+)-Ipomeamarone
(22)(±)-Ipomeamarone

(21)

obtained. This substance formed a semicarbazone of m.p. 122–123°, had infra-red absorption maximum at 5·89 μ (5·89 in ipomeamarone) and a strong bitterness, and it was assumed to be the expected substance (30).[25]



(23) (24) (25) (26) (27) (28) (29) (30)

Consequently, this procedure was adopted for the synthesis of ipomeamarone starting with β-furancarboxylic acid (31). Reactions (32) to (36) progressed similarly to the foregoing (23) to (28) to give (36). Attempted chlorination of the carboxylic acid (36) with thionyl chloride resulted in resinification, but chlorination was effected with oxalyl chloride. The reaction of the acid chloride (37) with di*iso*butylcadmium

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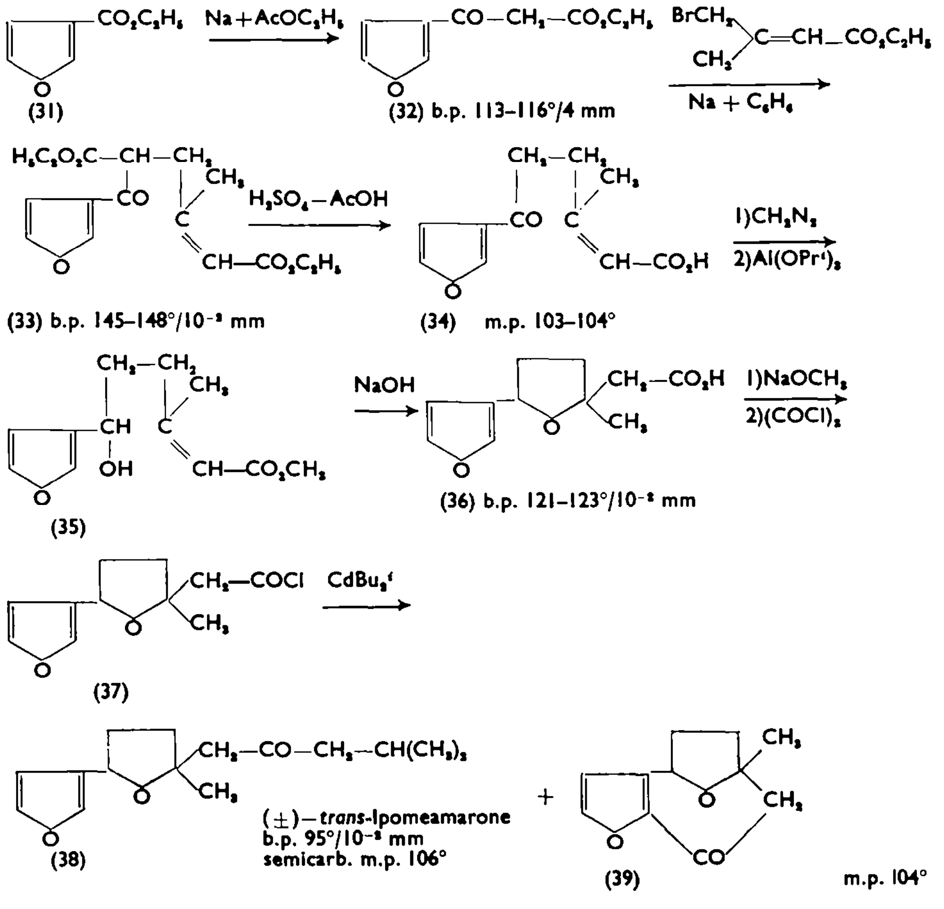
[25] T. Matsuura, *J. Chem. Soc. Japan* 77, 248 (1955).

gave a yellow liquid (38), b.p. 99–103°/10^{-3} mm, n_D^{11} 1·4910, assumed to be (±)-ipomeamarone, and (39), m.p. 103–104°. (38) possessed a strong bitter taste, its refractive index and colour reactions were the same as those of ipomeamarone, but its infra-red absorption curve, though similar, did not agree with that of ipomeamarone. Its semicarbazone melted at 104–106°, showing depression on admixture with the semicarbazone of natural (±)-ipomeamarone (22), and their infra-red spectra did not agree. It was therefore assumed that (38) is a stereoisomer of ipomeamarone. This stereoisomerism and the structure of (39) will be discussed in the next section. (38) boiled with acetic anhydride and potassium acetate was converted to the acetyl-*iso* compound (40) and its saponification and re-cyclization with alkali gave an oily substance (41). It formed a semicarbazone of m.p. 108–110°, which did not show any depression on mixing with the above-mentioned semicarbazone (m.p. 109·5–110·5°) of (22), and their infra-red absorption curves were completely in agreement.

The foregoing synthesis has definitely established the structure of ipomeamarone to be as represented by the formula (1).[26]



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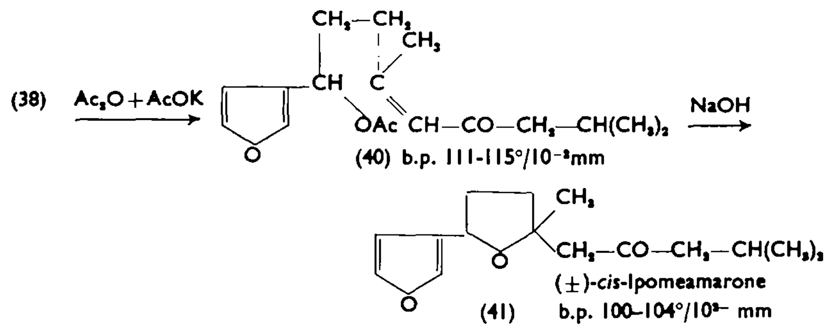
[26] T. Matsuura, *J. Chem. Soc. Japan* **78**, 389 (1956); T. Kubota and T. Matsuura, *Chem. & Ind.* 521 (1956); *J. Chem. Soc.* In press.



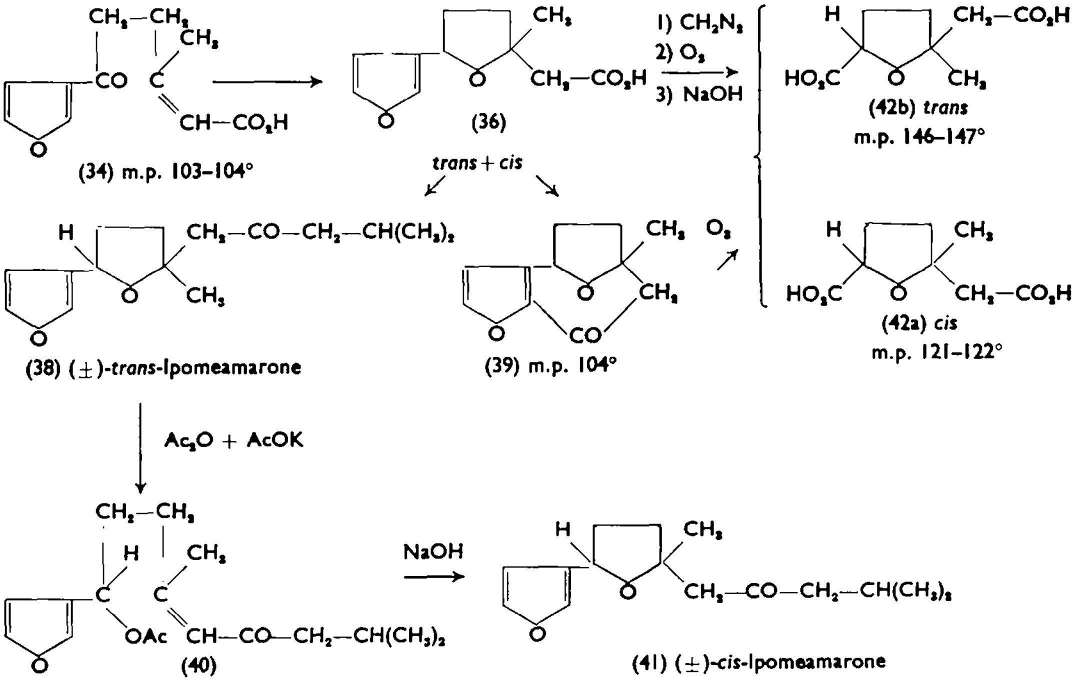
(38)

(40) b.p. 111-115°/10^{-3}mm

(41) (±)-*cis*-Ipomeamarone b.p. 100-104°/10^{-3} mm semicarb. 108-110° ≡ (22)—(semicarbazone)

Stereoisomerism of ipomeamarone[27]

During the course of the foregoing synthesis of ipomeamarone, application of di*iso*butylcadmium to the acid chloride (37) gave (38), assumed to be the stereoisomer of ipomeamarone, together with (39), m.p. 103–104°. This latter substance is a ketone, giving analytical values corresponding to $C_{11}H_{12}O_3$ (2:4-dinitrophenylhydrazone, m.p. 224°; semicarbazone, m.p. 239°) and is stable to mineral acids; the structural formula (39) is assumed for it. If this formula is correct, it would be sterically impossible for the ring containing the ketone group to be formed unless the furan ring and the carboxymethyl chain are in *cis* configuration. Therefore, the acid chloride (37) must be a mixture of steric isomers in which the side-chains at αα′-position of the tetrahydrofuran ring are in *trans* and *cis* configuration. The *trans* isomer would form (38) and the *cis* isomer would give the cyclic ketone (39).



(34) m.p. 103–104°

(36)

(42b) *trans* m.p. 146–147°

(38) (±)-*trans*-Ipomeamarone

(39) m.p. 104°

(42a) *cis* m.p. 121–122°

(40)

(41) (±)-*cis*-Ipomeamarone

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[27] T. Kubota and T. Matsuura, *J. Chem. Soc.* In the press.

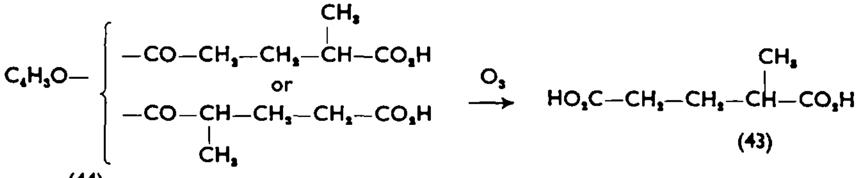
Now to prove whether this assumption is correct or not, the synthetic route for ipomeamarone was reviewed. The unsaturated keto-carboxylic acid (34), m.p. 104°, may be considered as sterically pure, and the carboxylic acid (36) obtained from it by cyclisation does not crystallise, but it is not possible to say whether it is a mixture of stereoisomers or an impure substance. Hence, (36) was submitted to esterification and ozonolysis, the product was saponified, and the acid obtained was fractionally crystallised, from which two crystalline carboxylic acids were obtained, one (42a) melting at 121–122° and the other (42b) at 146–147°. These acids gave the same analytical values ($C_8H_{12}O_5$) and neutralisation values, and were considered to be stereoisomers. Similar ozonolysis of the cyclic ketone (39), in which the furan ring and ketone side-chain are thought to be in *cis* configuration, gave the carboxylic acid (42a) of m.p. 121–122°, from which it is conceivable that (42a) has the *cis* structure and (42b) the *trans* structure.

This experiment has proved that the carboxylic acid (36) is a mixture of *cis* and *trans* isomers, and that the acid chloride (37) is also a mixture. This has also proved indirectly that (±)-*trans*-ipomeamarone (38) was derived from the *trans* acid chloride and the cyclic ketone (39) from the *cis* acid chloride. It may therefore be concluded that the natural (±)-ipomeamarone, obtained by the ring cleavage of (±)-*trans*-ipomeamarone with acetic anhydride and potassium acetate followed by re-cyclisation, is (±)-*cis*-ipomeamarone and the side-chains in natural (+)-ipomeamarone also have *cis* configuration (52).

Structure of batatic acid

Batatic acid is obtained as needle crystals of m.p. 88·5–89·5°, $[\alpha]_D$ 17·5°, in approximate yield of 0·0025 per cent of the sweet potatoes used. Analytical values and molecular-weight determinations suggest the molecular formula of $C_{10}H_{12}O_4$. It forms a mono-2:4-dinitrophenylhydrazone (m.p. 154·5–155·5°), monosemicarbazone (m.p. 177·5–178·5°), and mono-*p*-bromophenacyl ester (m.p. 94–95°). The neutralisation value corresponds to 1 mole of a compound of the above formula. Since its acetylation is impossible, the remaining oxygen must be neutral. Determination by the Kuhn–Roth method suggests the presence of one C-methyl group.

Ozonolysis of batatic acid gave a dicarboxylic acid of formula $C_6H_{10}O_4$, m.p. 81·5–82·5°, $[\alpha]_D$ 19·2°, which was assumed to be (+)-α-methylglutaric acid (43). Its identity was established by the synthesis of (±)-α-methylglutaric acid and by comparison of their infra-red absorption spectra. It follows, therefore, that batatic acid could be represented by (44).



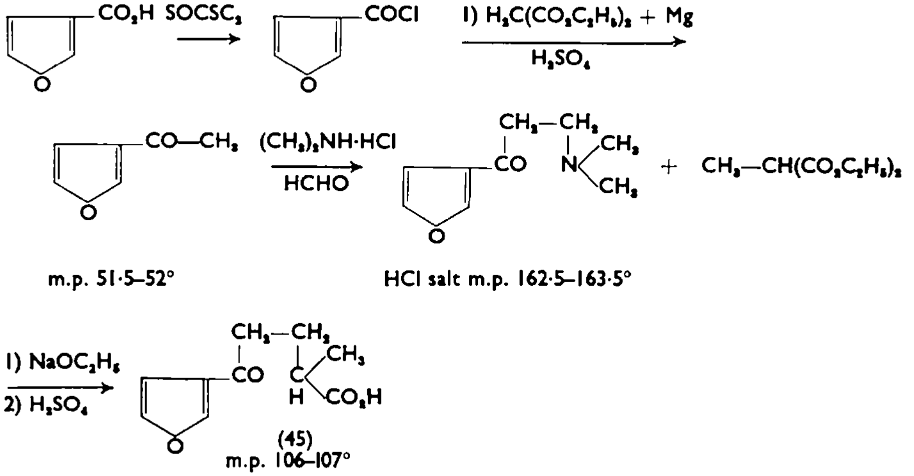
$$C_4H_3O-\left\{\begin{array}{l} -CO-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}H-CO_2H \\ \text{or} \\ -CO-\underset{CH_3}{\underset{|}{C}}H-CH_2-CH_2-CO_2H \end{array}\right. \xrightarrow{O_3} HO_2C-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}H-CO_2H$$

(44) (43)

The portion of formula C_4H_3O is thought to be a furan ring, but batatic acid is negative to the Ehrlich reaction, does not undergo addition with maleic anhydride and has a negative reaction for double bonds. This was assumed to be due to the stabilisation of the furan ring by the presence of a ketone in the α-position of the side-chain. Its reduction with lithium aluminium hydride converted it into a substance positive to all the above reactions. The correctness of this idea was confirmed with a few furan compounds.[28]

From the foregoing results and the fact that ipomeamarone and ipomeanine are present together in the black-rotted sweet potato, the structural formula (45) seemed to be the most probable[28] and this was proved by synthesis.

The synthesis of (45) was preceded by the synthesis of the corresponding compound possessing a benzene ring in place of a furan ring, i.e., α-methyl-γ-benzoylbutyric acid.[29] Subsequently, (±)-batatic acid (45) was synthesised as shown in the following scheme:



(45)
m.p. 106–107°

The infra-red absorption curve of synthetic (±)-batatic acid agreed completely with that of (+)-batatic acid, thus establishing the structure of (+)-batatic acid.[30]

Structure of ipomeanine[31]

Purification of the low-boiling fraction of the neutral portion from the ether extract of black-rotted sweet potato gave an oil of b.p. 74–79°/10^{-3} mm, n_D^{15} 1·4975, $[\alpha]_D$ + 3·86°. When the oil is inoculated with crystalline ipomeanine (synthetic), it crystallises with loss of optical activity. The decomposition experiment described below was carried out with an oily substance with $[\alpha]_D$ + 3–6°.

Ipomeanine gives analytical values corresponding to $C_9H_{10}O_3$ and forms a bis-2:4-dinitrophenylhydrazone, $C_{21}H_{18}O_9N_8$, m.p. 232–234°. Its reaction with semicarbazide is abnormal and the product is a dehydrated monosemicarbazone, $C_{10}H_{11}O_2N_3$, m.p. 215–216°. This could be explained by assuming that it is a reaction similar to that observed by Borsche *et al.*,[32] with 1:4-diketones. The semicarbazone would be represented by (46). Ipomeanine gives the iodoform reaction, suggesting

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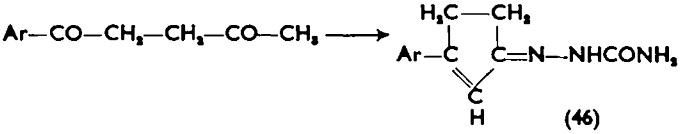
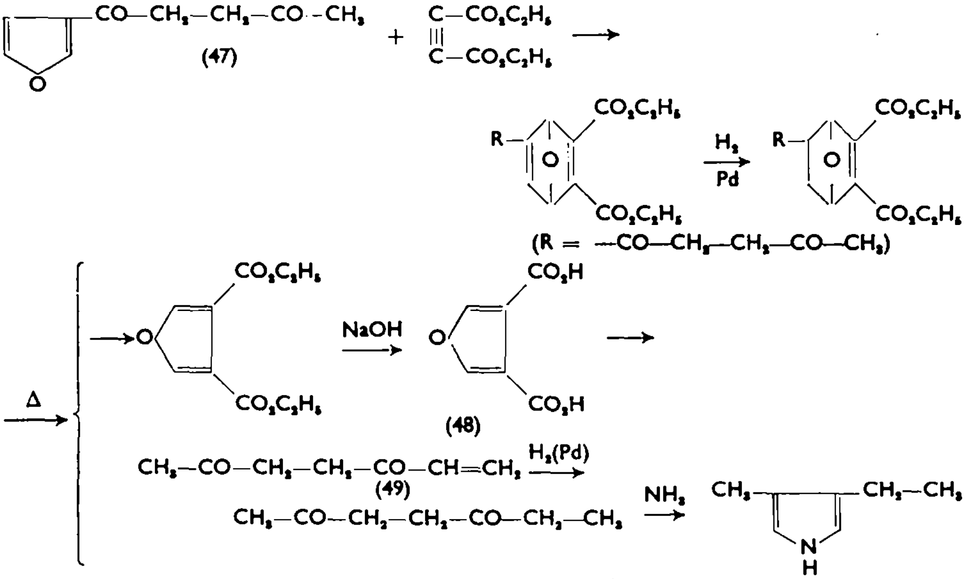
[28] T. Kubota and K. Naya, *Chem. & Ind.* 1427 (1954); *J. Chem. Soc. Japan* **77**, 86 (1955).
[29] K. Naya and T. Kubota, *J. Chem. Soc. Japan* **77**, 252 (1955).
[30] K. Naya, *J. Chem. Soc. Japan* **77**, 759 (1955).
[31] T. Kubota and N. Ichikawa, *Chem. & Ind.* 902 (1954); *J. Chem. Soc. Japan* **75**, 447 (1954)
[32] W. Borsche and W. Menz, *Ber. Dtsch. Chem. Ges.* **41**, 199 (1908).

the presence of a CH_3CO-type ketone. The remaining oxygen is assumed to be neutral from various colour reactions. Ipomeanine absorbed 2 moles of hydrogen by catalytic reduction to form tetrahydroipomeanine (semicarbazone, m.p. 174–175°) and reacted with maleic anhydride to give an addition product of m.p. 117–118°. Oxidation of ipomeanine with potassium permanganate gave levulic acid and ozonolysis gave levulic acid and formic acid. From the result of these oxidative decompositions, the colour reaction, the abnormality of its semicarbazone and the fact that this is a sub-component of ipomeamarone, the structure of ipomeanine could be assumed to be (47). In order to prove this, ipomeanine was submitted to an Alder–Rickert degradation. The reaction proceeded as expected, and furan-3:4-dicarboxylic acid (48) and a neutral unsaturated ketone (49) were obtained. Since the latter ketone gave a positive pine-splinter test after reduction of its double bonds and application of ammonia by forming a saturated ketone it seems almost certain that the structural formula (47) is correct.

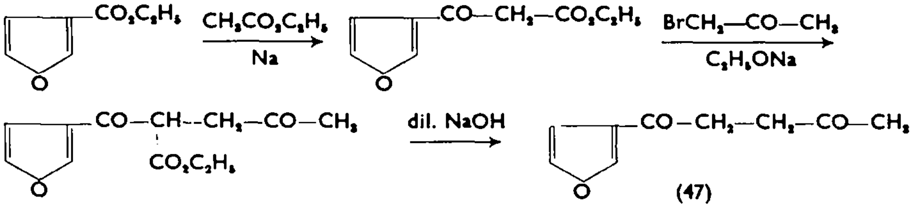


(46)



(47) (48) (49)

In order to prove this structure, synthesis of (47) was carried out by the following route.[31]:

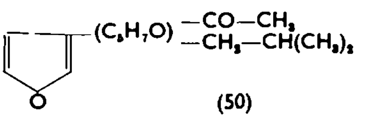


(47)

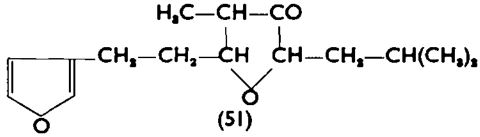
The synthesised product melted at 41–42°, and gave no depression of the melting point on admixture with the natural product; their infra-red absorption curves were in complete agreement.

Structure of ngaione

In 1925, McDowall[33] obtained a ketone, $C_{15}H_{22}O_3$, which he named ngaione, from the components of the essential oil from the leaves of a New Zealand shrub, *Myoporum laetum* Forst (called ngaio by the natives), and Brandt and Ross[34] gave it a partial structure (50) for it in 1949. Later, in 1953, Birch *et al.*[35] isolated ngaione from *Myoporum acuminatum* R. Br. and *Eremophila latrobei* (both found in Australia) and put forward the structure (51) for it.



(50)



(51)

As was also pointed out by Ohno,[36] physical constants of ipomeamarone and ngaione are similar, with the exception of optical rotations, as seen from the following data:

	b.p. (°C/mm)	n_D	d_4^{25}	$[\alpha]_D$	Semi-carbazone m.p. (°C)	$[\alpha]_D$
Ngaione	159–160/10	1·4769(25°)	1·0231	−25·1°(C_2H_5OH)		
				−12·3°(C_6H_6)	132·5–133	−66·2°
Ipomea-marone	145–149/5	1·4807(20°)	1·0290	+28·06°(C_2H_5OH)		
				+11·07°(C_6H_6)	133–134	+85°

The reactivity of these two substances was compared in co-operation with Birch and his co-workers and it was concluded that the two substances might be diastereoisomers.[37]

The chief basis for this assumption is the fact that the semicarbazone (8), $C_{13}H_{23}O_4N_8$ (the two active centres remain intact), of ipomeanic acid obtained by ozonolysis of the two ketones give different data, one from ipomeamarone melts at 167°, $[\alpha]_D$ −81° (in ethanol) and that from ngaione melting at 171–172°, $[\alpha]_D$ —40° (in ethanol).

It was later found that the infra-red absorption curves of the semicarbazones of ipomeamarone and ngaione were identical and it was concluded that these two substances are optical isomers. Considering the foregoing results on the synthesis of ipomeamarone, both ipomeamarone and ngaione should belong to the *cis*-system (52).[38] It is still not clear what causes the difference in the optical rotation of the semicarbazone of ipomeanic acid, but it may be possible that the semicarbazone

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[33] F. McDowall, *J. Chem. Soc.* 200 (1925); *Ibid.* 731 (1927); *Ibid.* 1324 (1928).

[34] C. W. Brandt and D. J. Ross, *J. Chem. Soc.* 2778 (1949).

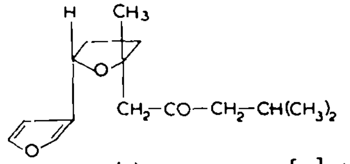
[35] A. J. Birch, R. Massy-Westropp and S. E. Wright, *Austr. J. Chem.* **6**, 385 (1953).

[36] T. Ohno, *Bull. Chem. Soc. Japan* **25**, 222 (1952).

[37] A. J. Birch, R. Massy-Westropp, S. W. Wright, T. Kubota and T. Matsuura, *Chem. & Ind.* 902 (1954).

[38] T. Kubota and T. Matsuura, *Chem. & Ind.* 521 (1956); *J. Chem. Soc.* In the press.

from ngaione is partially racemised, since the α-carboxylic acid of tetrahydrofuran is comparatively easily racemised.



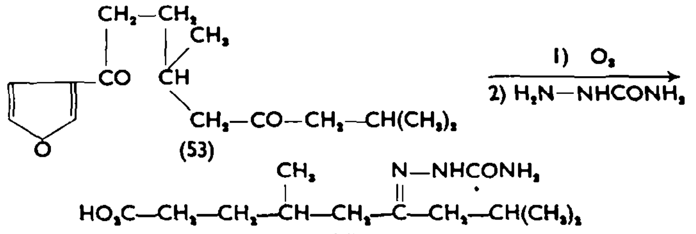
(52)

(+) Ipomeamarone: $[\alpha]_D$ + 28°
(−) Ngaione: $[\alpha]$ −25°

Component of Myoporum bontioides *and structure of myoporone*[39]

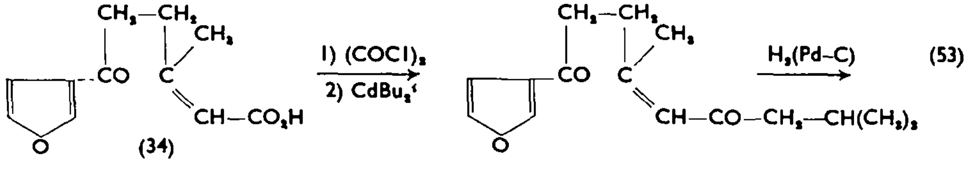
As was mentioned in the preceding section, studies have been made on the components of the essential oil of *Myoporum* spp. and ngaione and β-furancarboxylic acid[35] have been isolated. As a sample of ngaione was desired and some interest was felt for the components of the essential oil from the leaves of *Myoporum bontioides* A. Gray, the only Myoporum plant in Japan, an examination of this oil was made. Unexpectedly, however, only a minute amount of ngaione was found in the essential oil and the chief component was found to be an unknown ketone, $C_{15}H_{22}O_3$ (b.p. 117–119°/10^{-2} mm, n_D^{21} 1·4770, $[\alpha]_D$ 0°), which was named myoporone, and its structure was examined. Myoporone (53) forms two 2:4-dinitrophenylhydrazones, thought to be dimorphs:[40] a red α-compound of m.p. 193° and an orange-yellow β-compound of m.p. 193°, which turns reddish at 143–145°. Myoporone shows no optical rotation at the D-line, but its 2:4-dinitrophenylhydrazone (α-form) has $[\alpha]_D^{28}$ −28·2°. It gives a positive Ehrlich reaction and was assumed to have a structure closely related to that of ngaione.

Ozonolysis of myoporone afforded one keto acid whose semicarbazone, m.p. 139–141°, agreed with the semicarbazone (14), m.p. 141–142°, of dihydroanhydroipomic acid derived from ipomolactone. It may therefore be assumed that the structure of myoporone would be represented by (53).



(14)

In order to prove this assumption, the synthesis of myoporone was undertaken[39] from the keto-carboxylic acid (34), intermediate in the synthesis of (±)-ipomeamarone.



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[39] T. Kubota and T. Matsuura, *Chem. & Ind.* 491 (1957); *Bull. Chem. Soc. Japan* 31, 491 (1958).
[40] W. Dirscherl and H. Nahm, *Ber. Dtsch. Chem. Ges.* 73, 448 (1940).

TABLE 2. INFRA-RED ABSORPTION SPECTRA OF SUBSTITUTED FURANS

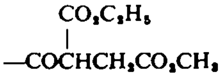
Substituents		Wavelength (μ)				
α	β					
—	—	3·16	6·33	6·91	11·47	13·79
$—CH_2OH$	—	—	—	6·64	11·31	13·4–13·6
$—CH_2OCOCH_3$	—	3·19	6·41	6·65	11·30	13·3–13·5
—CHO	—	3·16	6·40	6·82	11·32	13·10
—COOH	—	3·16	6·34	6·79	11·26	13·10
$—COOC_2H_5$	—	3·19	6·39	6·79	11·32 (11·52)	13·42
$—COCH_2CO_2C_2H_5$	—	3·18	6·37	—	11·30	13·00
 $—CO\overset{\overset{\textstyle CO_2C_2H_5}{\vert}}{C}HCH_2CO_2CH_3$	—	3·18	6·38	—	11·30	13·00
—	—COOH	—	6·40	6·64	11·42	13·00 (13·35)
$—CH_3$	—COOH	—	6·20	6·58	11·17	13·10 (13·50)
—	$—CO_2C_2H_5$	3·18	6·42	6·65	11·44	13·13
$—CH_3$	$—CO_2C_2H_5$	3·19	6·23	6·57	11·13	13·55
—	$—COCH_3$	3·21	6·41	6·63	11·44	13·13
—	—COOH —COOH	3·18	6·41	6·62	11·30	13·15
—	$—CO_2C_2H_5$ $—CO_2C_2H_5$	3·18	6·49	—	11·20	13·12
$—CO_2C_2H_5$ $—COCH_3$	—	?	?	?	?	13·10
$—COCH_3$	$—CO_2C_2H_5$	3·18	6·51	—	11·44	13·02
$—COCH_3$	$—CO_2C_2H_5$ $—CO_2C_2H_5$	3·18	6·51	—	11·24	13·00
$—CHOHCH_3$	$—CO_2C_2H_5$ $—CO_2C_2H_5$	—	—	—	11·23	13·12
—COOH —COOH	—COOH	—	—	—	11·24	?
—COOH —COOH	—COOH —COOH	—	—	—	11·52	13·20

TABLE 3. INFRA-RED SPECTRA OF FURAN DERIVATIVES

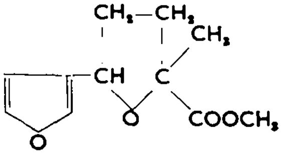
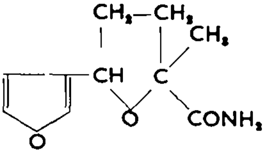
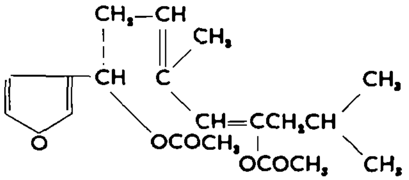
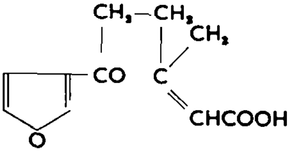
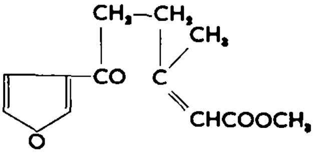
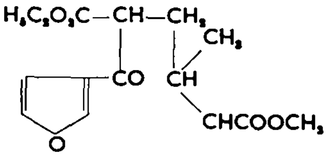
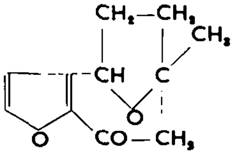
Compounds	Wavelength (μ)				
	3·19	—	6·62	11·42	12·60(?)
	3·19	6·41	6·65	11·37	12·60(?)
	3·19	6·40	6·63	11·42	13·62
	3·18	6·40	6·62	11·44	13·26
	3·18	6·40	6·62	11·44	13·42
	3·18	6·41	6·64	11·44	13·40
	3·21	—	6·67	11·32	13·13

TABLE 3 (continued)

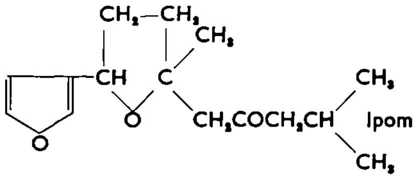
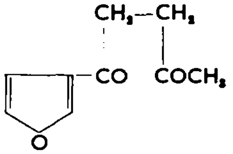
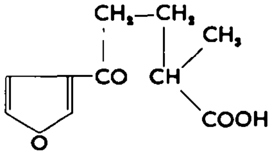
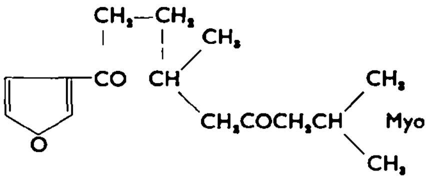
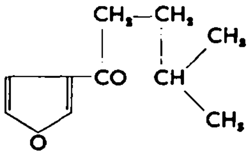
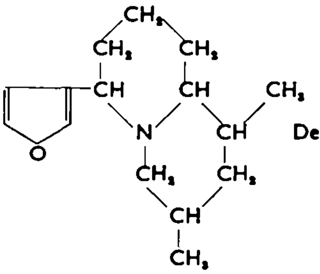
Compounds	Wavelength (μ)				
 Ipomeamaron	3·19	6·40	6·63	11·42	13·62
 Ipomeanine	3·19	6·40	6·62	11·44	13·30
 Batatic acid	3·20	6·40	6·62	11·46	13·20
 Myoporone	3·19	6·41	6·64	11·45	13·00
 Perilla ketone	3·18	6·40	6·63	11·45	12·90
 Desoxynupharidine	3·19	6·37	6·67	11·42	12·70, 13·08, 13·80
Columbin, $C_{20}H_{22}O_6$	3·19	—	6·65	11·42	12·73, 13·30

TABLE 3 (continued)

Compounds	Wavelength (μ)				
Limonin, $C_{26}H_{30}O_8$	—	—	6·66	11·44	13·16
Limonilic acid, $C_{26}H_{30}O_9$	3·18(?)	—	6·66	11·48	12·95
Methyl limonilate, $C_{27}H_{32}O_9$	3·20	—	6·66	11·46	12·97
Dehydrolimonin, $C_{26}H_{28}O_8$	3·13	—	6·66	11·45	13·13, 13·32
Limonin-$LiAlH_4$, $C_{26}H_{40}O_8$	3·12(?)	—	6·67	11·40	12·92
Limonin-$LiAlH_4$ acetate, $C_{34}H_{48}O_{12}$	3·18	—	6·67	11·40	12·93
Obacunone, $C_{26}H_{30}O_7$	3·18	—	6·66	11·42	13·12
Obacunone-$LiAlH_4$, $C_{26}H_{40}O_7$	?	—	6·72(?)	11·45	12·95

The bis(2:4-dinitrophenylhydrazone) of the synthetic product consists of red crystals, m.p. 208–210° (thought to be the α-compound), and the infra-red absorption spectra of the natural and the synthetic product were in complete agreement. It was thereby established that the structure of myoporone is represented by (53).

Infra-red absorption spectra of furan derivatives[41]

The following three bands have been selected as the characteristic absorption bands of the furan ring in this laboratory: (*a*) around 3·20 μ (C–H), (*b*) around 6·40 and 6·62 μ (aromatic ring) and (*c*) 11·3–11·5 μ (?).

The values around these absorption bands by various furan compounds investigated in this laboratory are indicated in Tables 2 and 3.

CONCLUSIONS

The foregoing experimental results have clarified the chemical composition of the components of black-rotted sweet potato and the components of the essential oil of *Myoporum bontioides* A. Gray, which are closely related. The chief substances that have been confirmed are (1), (45), (47), (52), (53) and β-furancarboxylic acid. Ipomeamarone, ngaione and myoporone are all normal sesquiterpenes in which the isoprene units are bonded in head-to-tail linkage, and the fact that the chain-end in these substances has cyclised to a furan ring is a specific characteristic. These are the first group of substances of this type of terpene to be found in nature (1951).

Ipomeamarone was formed as a result of abnormal metabolism in a sweet potato caused by the parasitic growth of *Ceratostomella fimbriata* and produced through consumption of its own starch.

Healthy sweet potatoes do not contain any furan compounds or terpenes,[11] no doubt through operation of the Krebs cycle, which has been shown by Uritani

[41] M. Yamaguchi, *Japan Analyst*, 7, 211 (1958).

and others[4] to take place when the cell functions in the sweet potato become abnormal through the effect of the fungus, the Krebs cycle being inhibited with the resultant formation of terpenes. Bonner, Lynen, Birch and others have studied the formation mechanism of terpenes from acetic acid through acetoacetic acid and mebalonic acid, and the results of these investigations may be applied to the formation of ipomeamarone during abnormal metabolism in the sweet potato.

On the contrary, ngaione and myoporone are considered to be the normal metabolic accumulation of a higher vegetable, *Myoporum*. The interesting point is that while the *dextro*rotatory (+)-ipomeamarone is accumulated in the black-rotted sweet potato, a *laevo*rotatory (—)-ngaione (= (—)-ipomeamarone) is accumulated by *Myoporum*. This may offer a key to elucidate the problem of biological reactions in the future.

Batatic acid, ipomeanine and β-furancarboxylic acid are considered to have been formed by the secondary oxidation of ipomeamarone in black-rotted sweet potatoes (or in *Myoporum* in the case of β-furancarboxylic acid), since their content is rather small. This cleavage of the side-chain is also an interesting problem and this mechhanism is a problem to be solved in the future.

Acknowledgements—I express my deep gratitude to Professor A. J. Birch, Manchester University, for supplying the sample of the semicarbazones of ngaione and for valuable discussions. I am also indebted to Miss Dorothy Mizoguchi for preparing the English manuscript.