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THE CONSTITUENTS OF *CACALIA DECOMPOSITA* A. GRAY. STRUCTURES OF MATURIN, MATURININ, MATURONE AND MATURINONE

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Abstract—The structures of maturin (IIa), maturinin (VI), maturone (VIIb) and maturinone (VIIa) have been established as furonaphthalene derivatives, closely related to cacalol (Ia) and cacalone (Ib).

RECENTLY, Cacalol (Ia) and cacalone (Ib), have been isolated from the extract of the roots of *Cacalia decomposita* A. Gray[2] and their structures established as furotetralin derivatives.[2,3] We wish now to report the isolation and structure proofs of four new products, isolated from the same source, which we propose to name *Maturin, Maturinin, Maturone and Maturinone* after the popular name of the plant, Maturin.[4] They are furonaphthalene derivatives closely related to cacalol (Ia) and cacalone (Ib).

Maturin, isolated from the benzene extract, is a yellow, crystalline product ($C_{16}H_{14}O_4$), m.p. 119–121°, optically inactive, (λ 251, 353 mμ; ϵ, 27000, 8550). The evidence cited below shows that maturin is a fully aromatic product represented by formula IIa.

Maturin (IIa) showed in the NMR spectrum,[5] singlets at 7·19 τ and at 5·55 τ (intensity three protons each), which could be assigned to C-methyl and methoxyl groups, respectively. The presence of both groups was confirmed by C-methyl and methoxyl determinations.

In the IR spectrum, maturin (IIa), showed the presence of an hydroxyl band at 3460 cm^{-1}, which disappears on acetylation. The NMR spectrum exhibited signals corresponding to an hydroxymethyl group, attached to a fully substituted carbon atom. A singlet at 5·94 τ (intensity one proton) which disappears on equilibration with deuterium oxide, was assigned to the hydroxyl proton: a splitted singlet at 5·27 τ (intensity two protons), which is shifted to a singlet at 4·70 τ on acetylation, corresponds to the methylene protons of the primary alcohol.

Maturin (IIa) possesses an α,β-unsaturated aldehyde group as shown by the following facts: It yielded an oxime. The IR spectrum had a band at 1660 cm^{-1} (unsaturated carbonyl group) and a NMR singlet at −0·83 τ (intensity one proton),

[1] Taken in part from a thesis by J. Correa, Universidad Nacional Autónoma de México.
[2] J. Romo and P. Joseph-Nathan, *Tetrahedron* **20**, 2331 (1964).
[3] P. Joseph-Nathan, J. J. Morales and J. Romo, *Tetrahedron*, in press.
[4] Maximino Martínez. Las Plantas Medicinales de México. Ediciones Botas, Mex. (1939).
[5] The NMR spectra were determined by Mr. Eduardo Díaz, on a Varian A-60 spectrometer, in $CDCl_3$. Tetramethylsilane was used as internal standard (t = 10·00).

ascribed to the aldehyde hydrogen. The aldehyde group could be reduced with LAH to an hydroxymethyl function, furnishing the dihydroderivative (IIIa), whose diacetate (IIIb) exhibited in the NMR spectrum, singlets at 4·71 and 4·19 τ (intensity two protons each) and two superimposed singlets at 7·90 τ (intensity six protons), corresponding two acetoxymethyl groupings.

Further proof of the presence of the aldehyde and hydroxymethyl functions in maturin (IIa), and information concerning their relative position as 1, 2 or 1, 3 was obtained by examination of the properties of the methylacetal (IVa) obtained from the mother liquors of maturin (IIa) and prepared by treatment of a methanolic solution of maturin (IIa) with hydrochloric acid. This derivative ($C_{17}H_{16}O_4$) did not show hydroxyl or carbonyl bands in the IR spectrum and did not form an acetate. It has two methoxyl groups (methoxyl determination), confirmed by the NMR spectrum, which exhibited two singlets at 6·34 and 5·59 τ (intensity three protons each), ascribed to two methoxyl groups. The chemical shift of the aldehyde hydrogen of maturin (IIa) has been displaced to higher field, at 3·53 τ, showing that now is involved in the acetal function.

The acetal (IVa) and those described below, though obtained from the extracts of the roots appear to be artifacts formed during the process of isolation, rather than products found in the plant.

The ethylacetal (IVb), isolated from the ethanolic extract of the plant was prepared by treatment of maturin (IIa) with ethanol and hydrochloric acid.

From an acetic acid solution of maturin (IIa), crystallized a product ($C_{32}H_{26}O_7$), isolated also from the benzene extract of the plant. The spectroscopic evidence indicates that this product is an acetal formed by condensation of two molecules of maturin as shown by formula V. Its IR spectrum had the aldehyde carbonyl band at 1660 cm^{-1}. The NMR spectrum showed four singlets at 7·25, 7·11, 5·58 and 5·55 τ (intensity 3 protons each) assigned to two C-methyl and two methoxyl groups. A complex signal centered at 4·83 τ (intensity four protons) corresponds to two methylene groups. The aldehyde and the acetal protons are responsible for two sharp singlets at −0·97 and 3·18 τ. A complex signal centered at 2·68 τ (intensity five protons), a singlet at 2·18 τ (intensity one proton) and a quadruplet centered at 1·67 τ (intensity two protons) are ascribed to the aromatic protons.

Maturin (IIa) has four aromatic hydrogen atoms as shown by the NMR spectrum. A triplet centered at 1·72 τ, a singlet at 2·22 τ (intensity one proton each) and a complex signal centered at 2·60 τ (intensity two protons).

The substituents already described appear to be attached to a furonaphthalene skeleton. This assumption is favoured by biogenetic considerations, since cacalol (Ia) and cacalone (Ib), isolated from the hexane extract, possess the same ring system. Furthermore, pyrolysis of the acetal (V) in the presence of palladium on charcoal afforded a dimethyl-methoxynaphthalene, characterized as its picrate.

The structure of maturin (IIa) was cleared up after consideration of the properties of maturone (VIIb), a product closely related to maturin (IIa).

Maturone (VIIb) is a yellow *p*-quinone ($C_{14}H_{10}O_4$), m.p. 169–170°, (λ max 250, 298, 354 mμ; ϵ, 29000, 6500, 3220), isolated from the benzene extract of the roots. It was correlated with maturin (IIa) when mild chromium trioxide oxidation of the acetal (V) afforded the same quinone (VIIb); its IR spectrum showed bands at 1670 cm^{-1} (quinonoid carbonyl groups). An IR band at 3500 cm^{-1} and the singlets in the NMR

spectrum at 5·23 τ (intensity two protons) and at 6·25 τ (intensity one proton), indicated the presence of the hydroxymethyl function. This substituent was not affected in the oxidation of the acetal (V), because in that reaction, the formate of the quinone (VIIc) was produced; only in the subsequent chromatographic purification was the formate (VIIc) partially hydrolyzed to the quinone (VIIb). Reductive acetylation of the quinone (VIIb) afforded the triacetate (VIIIb).

Maturone (VIIb) yielded an acetate (VIId), which could be obtained also by chromium trioxide oxidation of maturin acetate (IIb). Its IR spectrum had bands at 1740 cm^{-1} (acetyl group) and at 1670 cm^{-1} (quinonoid carbonyl groups).

The quinonealdehyde (IXa) was obtained by mild oxidation of maturone (VIIb) with chromium trioxide. A NMR singlet at $-0{\cdot}5\ \tau$ is attributed to the aldehyde hydrogen. Reductive acetylation afforded the triacetate (VIIIb). From the above oxidation a small amount of the acid (IXb) was obtained.

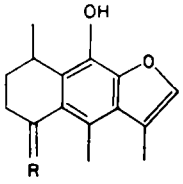
Oxidation of maturone with alkaline hydrogen peroxide, yielded 3-methylphthalic acid, characterized as its anhydride (X). Therefore the central ring of the furonaphthalene nucleus is responsible for the quinone chromophore; since the aldehyde and methoxyl groups of maturin (IIa) were eliminated in the degradative oxidation which produced maturone (VIIb), those functions were attached at that ring. Position 4 was assigned to the aldehyde group in order to explain the ease of acetalization with the hydroxymethyl substituent, which must be bonded at C-3, in the furan ring. Therefore, the methoxyl group is linked at C-9.

Reaction of maturone with thionyl chloride followed by treatment with sodium iodide furnished the iododerivative (VIIe). Reductive elimination of iodine of VIIe, afforded albeit in low yield, a product identical to maturinone (VIIa), a quinone isolated from the hexane extract of the roots. Maturin (IIa), maturone (VIIb) and maturinone (VIIa) were correlated with cacalol (Ia) and therefore their structure fully elucidated, when maturinone (VIIa), was found to be identical with the naphthofurandione obtained by oxidation of cacalol acetate with 2,3-dichloro-5,6-dicyanobenzoquinone, followed by treatment with chromium trioxide.[3]

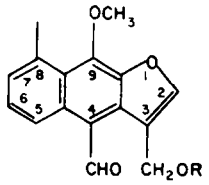
Maturinin (VI) ($C_{16}H_{14}O_3$), m.p. 95–96° (λ max 250, 372 mμ, ϵ, 28300, 8900) was isolated in small amount from the hexane extract of the roots; its spectroscopic features, very similar to those of maturin (IIa) indicated that this product is a furonaphthalene closely related to maturin (IIa) which possesses a C-3 methyl substituent instead of an hydroxymethyl grouping. The IR spectrum had a band at 1675 cm^{-1} (α,β-unsaturated aldehyde group). Two singlets in the NMR spectrum at 7·88 and 7·43 τ (intensity three protons each) showed the presence of two aromatic methyl groups. A methoxyl group is responsible for a singlet at 5·71 τ. A complex signal centered at 2·8 τ (intensity three protons) and a triplet centered at 1.94 τ (intensity one proton) were ascribed to four aromatic protons. A sharp singlet at $-0{\cdot}73\ \tau$ (intensity one proton), corresponds to the aldehyde hydrogen. Maturinin (VI) yielded an oxime.

Chromium trioxide oxidation of maturinin (VI) gave maturinone (VIIa). This result established the structure of maturinin (VI). Biogenetic considerations strongly suggest that the aldehyde function is attached at C_4 and the methoxyl group at C_9.

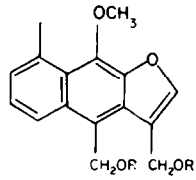
Maturinone (VIIa) and maturone (VIIb), appear to be the first naphthofurandiones known to occur in nature.



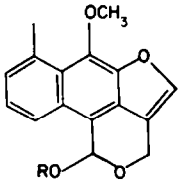
I a, R = H_2
b, R = O



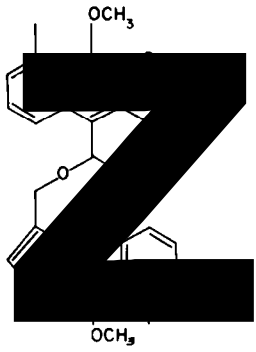
II a, R = H
b, R = Ac



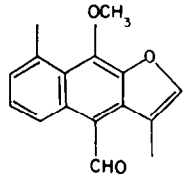
III a, R = H
b, R = Ac



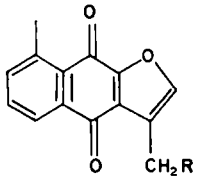
IV a, R = CH_3
b, R = C_2H_5



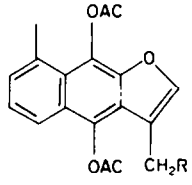
V



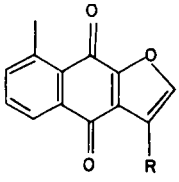
VI



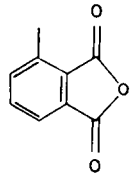
VII a, R = H
b, R = OH
c, R = HCOO
d, R = AcO
e, R = I



VIII a, R = H
b, R = AcO



IX a, R = CH = O
b, R = COOH



X

EXPERIMENTAL

Isolation of the furonaphthalene derivatives from Cacalia decomposita *A. Gray*

Maturinin (VI). The oily mother liquors (18 g), left after crystallization of cacalol and cacalone[a] were dissolved in hexane and chromatographed on 400 g of alumina. Several fractions eluted with

[a] M.Ps are uncorrected. The IR spectra were run in $CHCl_3$ solution on a Perkin–Elmer double beam spectrophotometer. The UV absorption spectra were determined in 95% EtOH solution on a Beckman DK2 spectrophotometer. The microanalyses, C-methyl, methoxyl values and MW determinations were performed by Dr. Franz Pascher, Bonn, Germany. Alumina Alcoa F-20 washed with AcoEt was used for the chromatography.

hexane crystallized. They were combined and recrystallized from acetone–hexane, this yielded yellow needles (140 mg), m.p. 95–96°, λ max 250, 372 mμ; ϵ, 28300, 8900; IR bands at 1675 cm^{-1} (aldehyde carbonyl group), 1615 cm^{-1} (C=C double bonds). (Found: C, 75·34; H, 5·53; O, 19·37. MW 257. Calc. for $C_{16}H_{14}O_3$: C, 75·57; H, 5·55; O, 18·88; OCH_3. 12·15. Calc. for one OCH_3 12·20%).

Maturinin oxime. Needles from aq EtOH m.p. 185°. (Found: C, 71·59: H, 5·67; O, 17·76; N, 5·41. Calc. for $C_{16}H_{15}O_3N$: C, 71·36; H, 5·61: O, 17·82; N, 5·20%).

Maturinone (VIIa). Elution with benzene–hexane 1:3 and 1:2 afforded crystalline fractions. They were combined and recrystallized from $CHCl_3$–MeOH; this yielded yellow needles (90 mg), m.p. 168–169°; λ max 246, 288 mμ; ϵ, 21500, 10000; IR bands at 1660 cm^{-1} (quinoniod carbonyl groups), 1580 cm^{-1} (C=C double bonds). Undepressed on admixture with the naphthofurandione obtained by oxidation of cacalol acetate with DDQ[8] the IR spectra were superimposable, identical Rf on TLC.

Maturone (VIIb). The powdered roots, after extraction with hexane,[8] were heated under reflux with 8 l of benzene for 24 hr. The benzene extract was evaporated to dryness and the residual brown oil (wt 35 g) dissolved in 2 l of benzene–hexane 1:1, was chromatographed on 700 g of alumina. The fractions eluted with benzene–hexane in different proportions left only oily residues, elution with benzene gave several crystalline fractions. They were combined and recrystallized from acetone–hexane and acetone–ether, this yielded yellow needles (2·5 g), m.p. 169–170°, λ max 250, 298 and 354 mμ; ϵ, 29000, 6500, 3260; IR bands at 3500 cm^{-1} (hydroxyl group), 1670 with a shoulder at 1690 cm^{-1} (quinonoid carbonyl groups), 1600 cm^{-1} (C=C double bonds). (Found: C, 69·51; H, 4·21; O, 26·45. MW 242. Calc. for $C_{14}H_{10}O_4$; C, 69·42; H, 4·16; O, 26·42%).

Mass spectrum of maturone gave MW 242; peaks at mass 224, 196 (base peak), 168, and 140, in accord with structure (VIIb).[7]

Maturone acetate (VIId). The acetate (VIId) was prepared by the acetic anhydride–pyridine method. Crystallization of the product from MeOH afforded yellow needles, m.p. 149–150°, λ max 252, 297 mμ; 17000, 6060; IR bands at 1740 cm^{-1} (acetyl group), 1670 cm^{-1} (quinonoid carbonyl groups), 1590 cm^{-1} (C=C double bonds). (Found: C, 67·43; H, 4·45; O, 28·31. MW 284. Calc. for $C_{16}H_{12}O_5$: C, 67·60; H, 4·26; O, 28·14%).

Mass spectrum of maturone acetate gave MW 284: peaks at mass 242, 224 (base peak), 196, 168 and 140.

Acetal (V). Elution with benzene and increasing proportions of ether, with ether and ether–$CHCl_3$ gave partially crystalline fractions. Crystallization of the combined fractions from acetone and $CHCl_3$-acetone, afforded (3·4 g) as yellow needles m.p. 201–203°, λ max 250, 338, 352 mμ; ϵ, 20100, 3330, 3400; IR bands at 1660 cm^{-1} (aldehyde carbonyl group), 1615 cm^{-1} (C=C double bonds). (Found: C, 73·24; H, 5·02; O, 21·77. MW 567. Calc. for $C_{32}H_{36}O_7$: C, 73·55; H, 5·02; O, 21·43; OCH_3: 11·83. Calc. for $2OCH_3$ 11·86%).

Maturin (IIa). The mother liquors left after the crystallization of V were evaporated. Crystallization from ether, yielded small yellow needles (1·4 g), m.p. 119–121°, λ max 251, 353 mμ; ϵ, 27000, 8550. IR bands at 3460 cm^{-1} (hydroxyl group), 1660 cm^{-1} (aldehyde carbonyl group), 1615 cm^{-1} (C=C double bonds). (Found: C, 71·14; H, 5·29; O, 23·64. MW 264. Calc. for $C_{16}H_{14}O_4$: C, 71·10; H, 5·22; O, 23·68; C-methyl 4·87; OCH_3 11·37. Calc. for one C-methyl 5·55, one OCH_3 11·47%).

Maturin oxime. Needles from benzene, m.p. 220–221°. (Found: C, 67·24; H, 5·11; O, 22·55; N, 5·09. Calc. for $C_{16}H_{15}O_4$: C, 67·36; H, 5·30; O, 22·43; N, 4·91%).

Maturin acetate (IIb). The acetate was prepared by the acetic anhydride–pyridine method. Crystallization from ether–hexane, yielded yellow needles m.p. 86°; IR bands at 1730 cm^{-1} (acetyl group), 1668 cm^{-1} (aldehyde carbonyl group). 1615 cm^{-1} (C=C double bonds). (Found: C, 69·42; H, 5·46; O, 25·54; MW 312. Calc. for $C_{18}H_{16}O_5$: C, 69·22; H, 5·16; O, 25·62%).

Maturin methylacetal (IVa). The oily residues left after evaporation of the mother-liquors of maturin, were dissolved in *methanol.* By concentration crystallized IVa (40 mg), as plates m.p. 150–151°, λ max 218, 250, 335, 349 mμ; ϵ, 16300, 65000, 10000, 8700. The IR spectrum did not show hydroxyl or carbonyl bands. (Found: C, 72·02; H, 5·52; O, 22·55. Calc. for $C_{17}H_{16}O_4$: C, 71·82; H, 5·67; O, 22·51; OCH_3, 21·98. Calc. for $2OCH_3$ 21·81%).

Maturin ethylacetal (IVb). After the extraction of the roots with benzene, the material was heated under reflux with EtOH (81.) for 24 hr. The ethanolic extract was evaporated to dryness and the oily residue (40 g) extracted twice with hot benzene. The benzene extract was chromatographed on

[7] Mass spectra were run by the Institut de Chimie des Substances Naturelles, Gif-sur-Ivette, France, through the courtesy of Prof. E. Lederer, to whom we are indebted.

alumina (200 g) and the crystalline fractions obtained, were combined. Crystallization from acetone–hexane yielded 450 mg, m.p. 100–101°, λ max 218, 250, 335, 350 mμ; ϵ, 13800, 55000, 8300, 8900. The IR spectrum did not show hydroxyl nor carbonyl bands. (Found: C, 72·20; H, 6·06; O, 21·71; MW 316. Calc. for $C_{18}H_{16}O_4$: C, 72·46; H, 6·08; O, 21·46%).

Acetal (V), *from Maturin* (IIa). Maturin (IIa, 260 mg) was dissolved in hot acetic acid (4 ml). After a few min the solution crystallized; it was then diluted with water, the precipitate collected and washed with water. Crystallization from acetone, yielded yellow needles (200 mg), m.p. 202–203°. Undepressed on admixture with V obtained from the extract of the roots, the IR spectra were superimposable.

Maturin methylacetal (VIa) *from maturin* (IIa). A solution of IIa (240 mg) in $CHCl_3$ (10 ml) and MeOH (20 ml) was treated with 20% HClaq (5 ml) and heated under reflux for 15 min. IVa crystallized from the solution upon concentration, this yielded 150 mg, m.p. 150–151°. It was identified by the standard methods with the methylacetal obtained from the mother liquors of maturin. When V was treated with HCl under similar conditions, IVa, (m.p. 150–151°) was obtained.

Maturin ethylacetal (IVb) *from maturin* (IIa). In a similar way, using EtOH, IVa was prepared, m.p. 100–101°. It proved to be identical with that isolated from the ethanolic extract.

Dihydromaturin (IIIa). A solution of IIa (100 mg) in anhydrous ether (30 ml) was treated with LAH (200 mg) and the mixture heated under reflux (2 hr). The excess LAH was decomposed with ethyl acetate and water and the etheral solution washed with dil. HClaq, water and evaporated. Several crystallizations from ethyl acetate–hexane, afforded needles (40 mg). m.p. 175–177°; λ max 249, 332, 348 mμ; ϵ, 66300, 9150, 8100; the IR spectrum did not show a carbonyl band. (Found: C, 70·81; H, 5·74; O, 23·44. Calc. for $C_{16}H_{16}O_4$: C, 70·57; H, 5·92; O, 23·50%).

Dihydromaturin diacetate (IIIb). Acetylation of IIIb with pyridine–acetic anhydride and crystallization of the product from ether, afforded needles, m.p. 143·5–144·5°; IR bands at 1735 cm^{-1} (acetyl groups). (Found: C, 67·37; H, 5·74; O, 26·99. Calc. for $C_{20}H_{20}O_6$: C, 67·40; H, 5·66; O, 26·94%).

Chromium trioxide oxidation of the acetal (V). To a solution of V (500 mg) in acetic acid (180 ml), a solution of CrO_3 (450 mg) in water (2 ml) and acetic acid (2 ml) was added with mechanical stirring. The temp was kept below 15°. The mixture was then left at room temp for 1 hr, water (600 ml) was added and the precipitate collected and washed with water. The dried product dissolved in benzene was chromatographed on alumina. From the less polar fractions eluted with benzene, VIIc (30 mg) was obtained. The analytical sample showed m.p. 170–171° (needles from ethyl acetate): IR bands at 1725 cm^{-1} (ester group), 1670 cm^{-1} (quinonoid carbonyl groups), 1590 cm^{-1} (C=C double bonds); NMR singlet at 1·77 t (formyl proton); (Found: C, 66·26; H, 4·13; O, 29·66. Calc. for $C_{18}H_{10}O_6$: C, 66·67; H, 3·73; O, 29·60%).

The more polar fractions eluted with benzene and benzene-ether were combined and recrystallized from benzene–hexane: this yielded yellow needles (170 mg), m.p. 169–170°, undepressed on admixture with VIIb, the IR spectra were superimposable.

Chromium trioxide oxidation of maturin acetate I(b). A solution of Ib (125 mg) in acetic acid (5 ml) was oxidized with CrO_3 (100 mg) in water (0·5 ml). Crystallization from MeOH yielded yellow needles (85 mg), m.p. 150°, undepressed on admixture with VIId: the IR spectra were superimposable.

Reductive acetylation of maturone (VIIb). A solution of 100 mg of VIIb in 2 ml of acetic anhydride, containing 50 mg of anhydrous sodium acetate and 510 mg of powdered Zn, was heated under reflux for 45 min, diluted with water and extracted with ethyl acetate. The organic extract was washed with 5% NaOHaq, water and evaporated to dryness. Crystallization from acetone–hexane, afforded VIIIb as white needles (105 mg), m.p. 171–172°; λ max 140, 246, 318, 344 mμ; ϵ, 68000, 72700, 10500, 8300. IR bands (KBr) at 1755 with a shoulder at 1730 cm^{-1} (acetyl groups), weak bands at 1650 and 1600 cm^{-1} (C=C double bonds). (Found: C, 65·47; H, 4·88; O, 29·89. Calc. for $C_{20}H_{18}O_7$: C, 64·86; H, 4·90; O, 30·24%).

Chromium trioxide oxidation of maturone (VIIb). A solution of VIIb (300 mg) in acetic acid (8 ml) was treated with CrO_3 (300 mg) in 50% aq acetic acid (2 ml) for 30 min, diluted with ice water and extracted with $CHCl_3$. The organic layer was washed with water, extracted with $NaHCO_3$aq and evaporated to dryness. Crystallization of IXa from acetone, afforded yellow needles (yield 160 mg), m.p. 215–217°; λ max 252 mμ; ϵ, 23000; IR bands at 1670 cm^{-1} (quinonoid and aldehyde carbonyl groups), 1585 cm^{-1} (C=C double bonds). (Found: C, 70·16; H, 3·10; O, 26·88; MW 243. Calc. for $C_{14}H_8O_4$: C, 70·00; H, 3·36; O, 26·64%).

The $NaHCO_3$aq solution was acidified with dil. HClaq and extracted with $CHCl_3$. The organic layer was washed with water and evaporated. Crystallization from $CHCl_3$–hexane afforded IXb, m.p. 238° (prisms from $CHCl_3$–hexane); IR bands at 1740 cm^{-1} (carbonyl group), 1680 (quinonoid carbonyl groups), 1640 and 1585 cm^{-1} (C=C double bonds). (Found: C, 64·94; H, 3·12; Calc. for $C_{14}H_8O_5$: C, 65·63; H, 3·15%).

Reductive acetylation of IXa was carried out as above. The product proved to be identical with VIIIb.

Hydrogen peroxide oxidation of maturone (VIIb). A solution of VIIb (200 mg) and 40% H_2O_2 (3 ml) in MeOH (30 ml) was treated with KOH (700 mg) in water (2 ml). The mixture was refluxed for 20 min concentrated to a small volume, diluted with water, acidified with dil HClaq and extracted with ether. The ethereal extract was evaporated to dryness and the oily residue sublimed in high vacuum. Crystallization from acetone–hexane, yielded 3-methylphthalic anhydride (40 mg); m.p. 114–115°; IR bands at 1850 and 1780 cm^{-1} (anhydride group), at 1628 cm^{-1} (C=C double bonds). It proved to be identical with an authenic specimen,* (Found: C, 66·42; H, 3·84; O, 29·62. Calc. for $C_9H_6O_3$: C, 66·67; H, 3·37; O, 29·60%).

Iodoquinone (VIIe). A solution of VIIb (150 mg) in $SOCl_2$ (5 ml) was heated under reflux for 20 min and evaporated to dryness *in vacuo*. The solid residue, dissolved in 15 ml acetone was treated with 1 g NaI, heated under reflux for 2 hr, poured in water and extracted with ether. The ethereal extract was washed with water, $NaHSO_3$aq and evaporated. Crystallization of the residue from acetone–hexane, afforded VIIe (yield 80 mg), as prisms m.p. 202–204°; IR bands at 1670 cm^{-1} (quinonoid carbonyl groups), at 1600 cm^{-1} (C=C double bonds). The NMR spectrum exhibited a singlet at 7·08 τ (intensity 3 protons) (aromatic methyl group), a sharp singlet at 5·30 τ (intensity 2 protons) (hydrogens of the iodomethyl group). A quadruplet centered at 1·72 τ a singlet at 2·08 t (intensity 1 proton each) and a complex signal centered at 2·33 τ (intensity 2 protons), (aromatic hydrogen atoms). (Found: C, 47·93; H, 2·99; Calc. for $C_{14}H_9O_3I$: C, 47·63; H, 2·57%).

Zinc reduction of the quinone (VIIe). A solution of VIIe (60 mg) in acetic acid (6 ml) was heated with powdered Zn (1 g) on the steam bath for 3 hr, filtered, diluted with water and extracted with $CHCl_3$. The organic layer was washed with $NaHCO_3$aq water, evaporated and the residue (40 mg) chromatographed an alumina. The first crystalline fractions eluted with benzene were combined. Crystallization from acetone–hexane afforded VIIa (10 mg), m.p. 163–165°. Undepressed on admixture with a sample of maturinone, the IR spectra were superimposable, TLC showed the same Rf.

Aromatization of the acetal (V). An intimate mixture of V (1·5 g) and 10% Pd-C (2 g) was heated for 1 hr at 320°, followed by extraction with benzene. The benzene extract was evaporated to dryness; the residue dissolved in MeOH was treated with picric acid. Upon concentration the picrate crystallized as brown plates (150 mg). m.p. 144–145°. (Found: C, 55·28; H, 3·94; O, 31·02. Calc. for $C_{19}H_{17}O_8N_3$: C, 54·94; H, 4·13; O, 30·82%).

Extraction of the picrate with NH_4OH afforded an oily product, which did not crystallize after chromatography on alumina. The NMR spectrum is in accord with a dimethyl-methoxy-naphthalene structure; it showed singlets at 7·75, 7·30 and at 5·68 τ (intensity three protons each), ascribed to 2 aromatic methyl groups and a methoxyl grouping respectively. A triplet centered at 1·78 τ, a singlet at 2·32 τ (intensity 1 proton each) and a complex signal centered at 2·68 τ (intensity 3 protons) correspond to the aromatic protons of the naphthalene nucleus.

Chromium trioxide oxidation of maturinin (VI). Compound VI (100 mg) in acetic acid (4 ml) was oxidized with a solution of CrO_3 (110 mg) in water (0·5 ml). Crystallization from acetone–hexane, afforded VIIa, as yellow needles (yield 45 mg), m.p. 168–169°. It proved to be identical with maturinone obtained from the extract of the roots VIIIa.

Reductive acetylation of VIIa yielded VIIa, m.p. 202–204°. IR bands at 1770 cm^{-1} (acetyl groups) weak bands at 1650 and 1585 cm^{-1} (C=C double bonds). (Found: C, 69·20; H, 5·05; O, 25·34. Calc. for $C_{18}H_{16}O_5$: C, 69·22; H, 5·16; O, 25·62%).