

Structures of some unusual types of organic compounds

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Abstract. Structures of a variety of compounds isolated in reactions and elucidated with the help of spectral (UV, IR, NMR and mass) data, have been discussed. In a few cases, the assigned structures were confirmed by x-ray crystal structure analysis.

Keywords. Steroids; seco-steroids; abietic acid; mass spectrum; infrared; acylation; alkylation; isoxazole; cyclisaton; oxidation; halogenation; x-ray crystallography.

1. Introduction

Chemistry of natural products including structure determination has attracted wide attention. With the innumerable number of new classes of compounds isolated and identified, it is hard to look for new classes of compounds. Further, competition is quite keen. However, quite often, reactions in the laboratory produce minor amount of byproducts or sometimes major amount of unexpected products. Isolation and determination of structures of these products are quite challenging and the nature of the byproducts, quite often, throws much light on the mechanism of the reaction. Also, elucidation of the structures of these products helps in developing new chemistry. It is thus rewarding to look carefully into minor products obtained in organic reactions. With the modern techniques of separation (TLC, HPLC and GLC) available, it is not that difficult to separate and purify organic compounds. In the following pages, the structures of a variety of compounds are discussed, some simple and others complex (isolated in reactions) elucidated with the help of spectral data. In a few cases, the structures proposed have been confirmed by x-ray crystal structure analysis.

2. Discussion

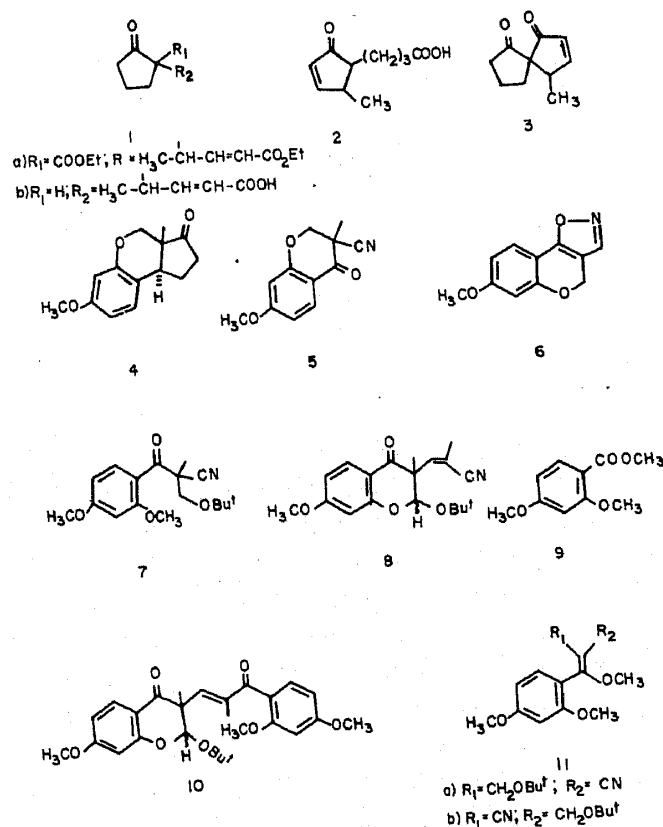
2.1 *Rearrangement during acid hydrolysis*

As a model study for the introduction of the bile acid side chain by the condensation of ethyl 4-bromo-2-pentenoate with a suitable β -keto ester derivative followed by hydrolysis and decarboxylation, we had condensed the above unsaturated bromo ester with 2-carbethoxycyclopentanone to obtain the substituted keto ester (**1a**). Herz (1956) had shown earlier that such condensation products, after reduction, yielded rearrangement products on treatment with conc hydrochloric acid. When the condensation product (**1a**) was treated under Herz's condition, a mixture of the normal acid (**1b**) and the rearranged acid (**2**) was obtained. The structure of the rearranged acid was evident from its uv spectrum. When the condensation product was treated with a more dilute acid *viz* 10% sulphuric acid, the normal product could be obtained in 93% yield. The above results could be explained on the basis of formation of a spirodiketone (**3**) in the

presence of strong acids. The spirodiketone (3) could open either way to give rise to the mixture of rearranged (2) and normal (1b) products.

2.2 Products of isomerization of isoxazole

In connection with the synthesis of 11-oxasteroid analogs, a stereospecific synthesis of a key intermediate (4) using the well-known benzhyrindane approach for the construction of *transfused* C/D rings (Johnson *et al* 1947; Banerjee *et al* 1956) was required. The starting material for this synthesis was the cyanomethyl chromanone (5). We anticipated that this could be easily synthesised from the corresponding isoxazole (6) following Johnson's procedure for the carbocyclic analog (Johnson *et al* 1945). When the isoxazole (6) was treated with potassium-*t*-butoxide in *t*-butanol at 75–80° (10 min) followed by treatment with methyl iodide and refluxing for 10 hr, a number of products were formed. The required cyanomethyl ketone (5) was formed in small amounts. The mixture of products could be separated by careful column chromatography followed by thin layer chromatography. A detailed study of the UV, IR, NMR and mass spectra of these compounds suggested their structures to be 7–11. The formation of these products was explained through the base-catalysed ring opening of the chroman ring after isomerization of the isoxazole (Kasturi and Damodaran 1966; Kasturi *et al* 1970a, b, 1975, 1976). The occurrence of sharp signals at δ 1.1 (4.5H), 1.28 (4.5H), 3.7 (1H) and 4.24 (1H) in the NMR spectrum of 11, which is apparently anomalous, is best explained by assuming it to be a mixture of fortuitously equal amounts of geometrical isomers (11a and 11b). The isomers could not, however, be separated. The peaks at δ 1.1 and 3.7 were assigned respectively to the *t*-butyl and oxymethylene groups shielded by



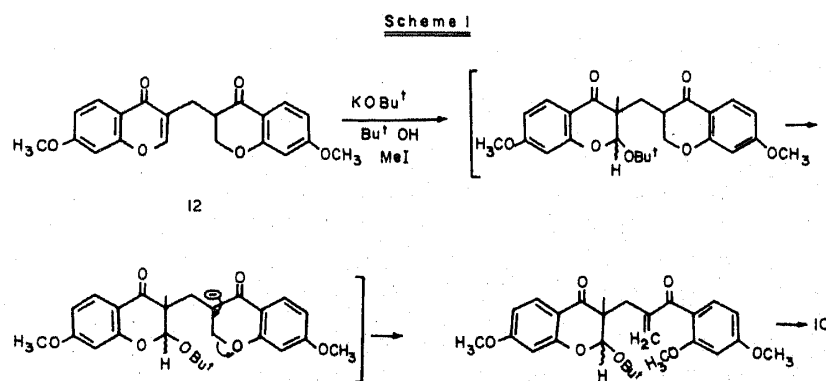
the aromatic ring in the isomer 11a and those at δ 1.28 and 4.24 to the *t*-butyl and oxymethylene groups in the isomer 8b (Kasturi *et al* 1970). By employing weaker bases like NaOEt, NaOMe or NaOCH(CH₃)₂ the keto nitrile (5) was obtained as the major product (Kasturi *et al* 1976). Further, the structure of one of the products (10), was confirmed by an alternate synthesis from the chromano-chromanone (12) obtained as a byproduct in the formylation of 7-methoxychroman-4-one as indicated in scheme 1 (Kasturi *et al* 1970).

2.3 Dehydrogenation studies with methyl abietate

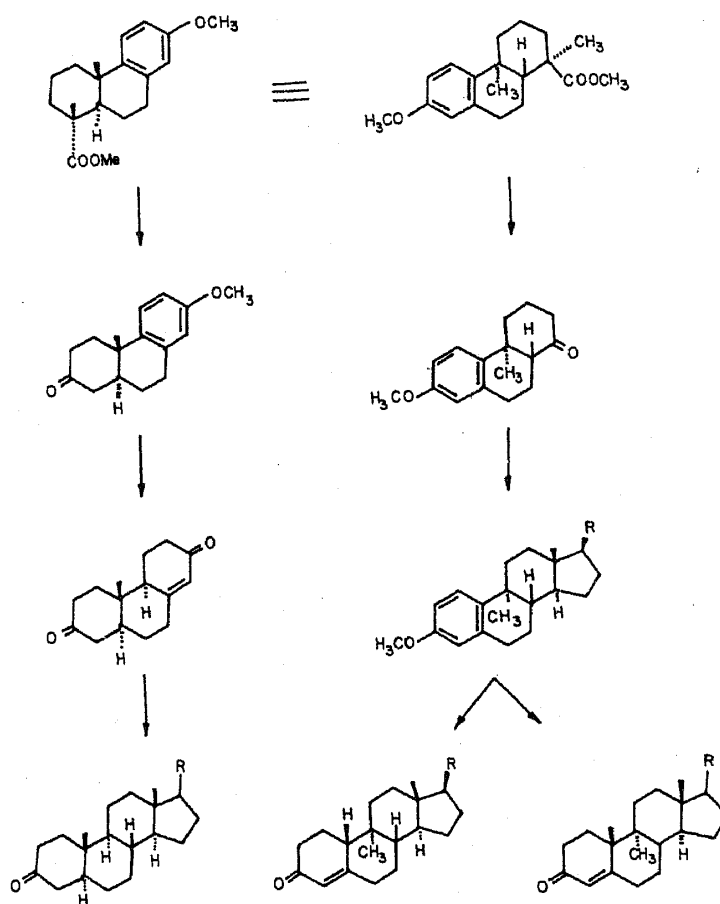
Methyl 13-hydroxydeisopropyldehydroabietate (13a) prepared earlier by Wenkert *et al* (1961), Burgstahler and Worden (1961) and Cambie and Franich (1971) from abietic acid in a low overall yield involving a large number of steps, is a key intermediate (scheme 2a) for the synthesis of natural as well as modified steroids (Banerjee and Kasturi 1971). We could synthesise the same (13a) by a novel shorter route in a considerably more improved yield utilising an adduct obtained in the reaction of methyl abietate with tetrachloro-*o*-benzoquinone (*o*-chloranil) (Kasturi *et al* 1966).

With a view to bring about the dehydrogenation of methyl abietate to methyl dehydroabietate (13b), the reaction of methyl abietate with 1 mole of *O*-chloranil in benzene was carried out. Instead of the expected product, a solid ester in 41% yield was obtained. This on hydrolysis with 10% butanolic potassium hydroxide gave the corresponding acid (14b). Diazomethane esterification of the acid (14b) gave back the original ester (14a). Hydrogenation of the solid ester gave a tetrahydro derivative. The presence of 4 chlorine atoms (isotopic cluster in mass spectrum) and the UV absorption maximum at 236 nm characteristic of abieta-diene system (Rao 1961), indicated that this could be an adduct. A detailed study of the NMR spectrum of the solid confirmed the structure as 14a, which could also be converted into the corresponding dehydroabietate derivative (15) by treatment with *O*-chloranil. The formation of the adduct (14a) could be rationalized by a dehydrogenation addition mechanism (Banerjee *et al* 1968). The increase in the yield of the adduct to 80% by using 2 moles of the quinone for one mole of methyl abietate lends support to it. Further, similar treatment of limonene gave an addition compound (16) which was also obtained from *p*-cymene and this seems to be a general method for functionalisation of an isopropyl group on an aromatic ring or an ethylenic linkage.

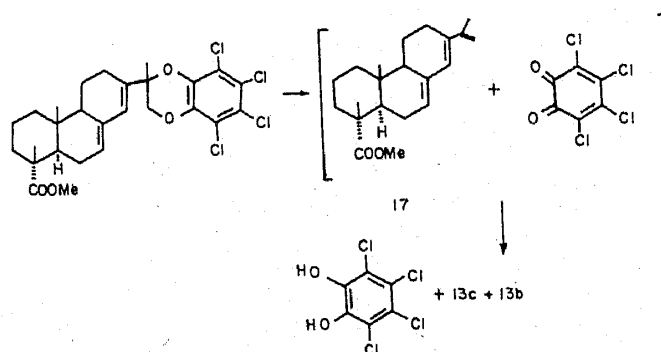
In view of the formation of the adduct in good yield, attempts were made to utilise this for the synthesis of the key intermediate (13a). A perusal of the mass spectrum of



Scheme 2a



Scheme 2b

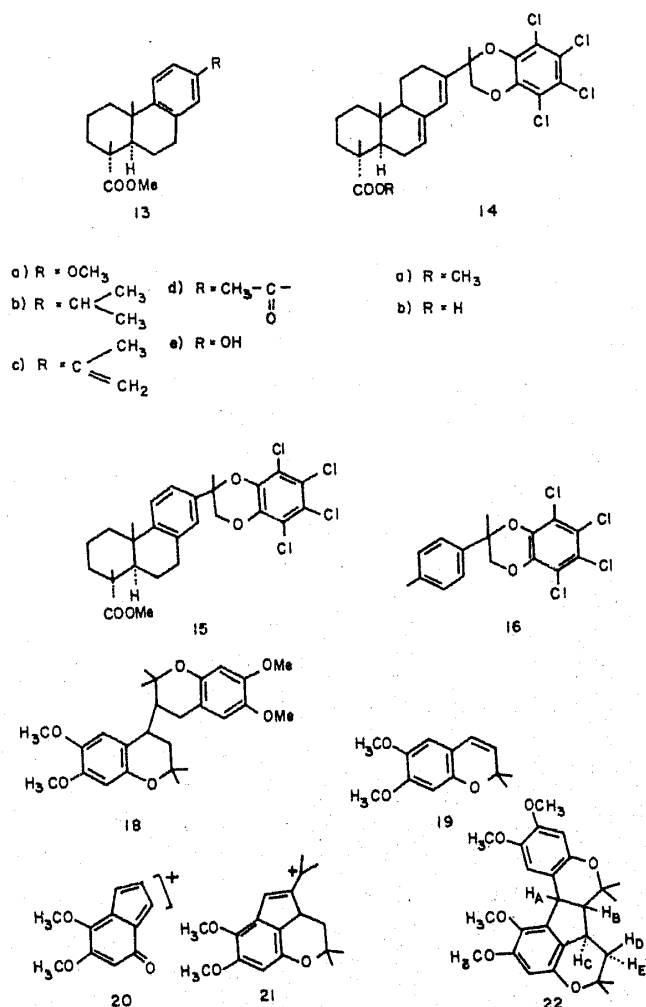


the adduct (13a) indicated that the retro-Diels-Alder fragment at m/z 314 was the base peak. This led us to study the thermal decomposition of the adduct (13a) which yielded a mixture of the styrene derivative (13c) and methyl dehydroabietate (13b). A probable mechanism of formation of the pyrolysis product consists (scheme 2b) of the reversal of the adduct formation at the high temperature followed by dehydrogenation of the triene (17) with the generated quinone to give the styrene (13c) and the hydroquinone

and partly by the rearrangement of **17** to give methyl dehydro-abietate (**13b**) (Banerjee *et al* 1968).

2.4 Dimer of ageratochromene

We have reported (Kasturi and Manithomas 1967) the isolation of a dimer (**18**) of ageratochromene (**19**) from the essential oil of *Ageratum conyzoides*. In order to prove its structure, the same compound (**18**) was synthesised by dimerisation of ageratochromene (**19**) with methanolic hydrochloric acid or mixture of acetic-sulfuric acid. Another solid obtained in this reaction was also shown (spectral data) to be a dimer of ageratochromene (Kasturi *et al* 1973). The NMR spectrum showed the presence of only three aromatic protons (sharp singlets at δ 6.25, 6.37 and 7.3) and no olefinic protons. The 60 and 100 MHz spectra of this solid showed a doublet at δ 4.45 (1H) with the same separation (7 Hz) in each case; this must arise from a single nucleus, probably a doubly benzylic proton. The separation of the three singlets (12H) at δ 3.78, 3.81 and 3.90 in the 60 and 100 MHz spectra are in the ratio 6:10; hence, these signals must be due to four methoxy groups. The four methyl signals at δ 1.27, 1.35, 1.43 and 1.5 are distinct and show no coupling to any other protons; their separations at 60 and 100 MHz are in the expected ratio of 6:10. These methyl groups must arise from two gem-dimethyl groups.



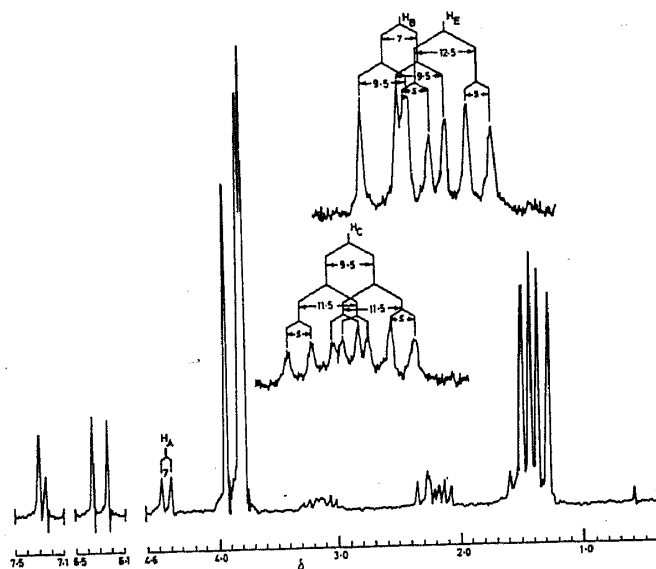


Figure 1. PMR spectrum of dimer (22)

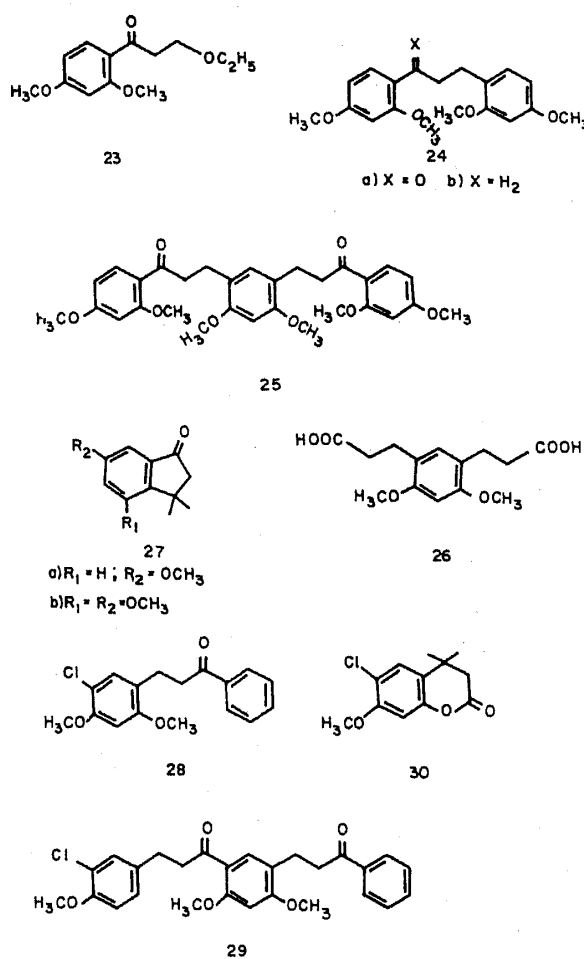
On the basis of the mass spectral fragments m/z 287 (20) and 231 (21), and on the basis of spin decoupling experiments (figure 1), a cyclopentabenzopyran structure (22) was proposed (Kasturi *et al* 1973). The splitting pattern of the protons H_A , H_B , H_C , H_D and H_E in (22) was similar to that in isolapachenole (23) (Cotterill *et al* 1968). A suitable mechanism to explain the formation of this dimer (22) has been proposed.

2.5 Reactions of 1,3-dimethoxybenzene derivatives

Acylation of 1,3-dimethoxybenzene with 3-ethoxypropionic acid using polyphosphoric acid at 40° for 3–5 minutes was expected to give 23. Compound 23 was not formed in the reaction. However, two ketonic substances designated A and B were isolated. Ketone A, M^+ m/z 330, showed in NMR 4 methoxy signals [δ 3.81, S(6H) and 3.87, S(6H)] and was assigned structure 24a. The desoxo compound (24b) obtained by hydrogenolysis with diborane was synthesised by an unambiguous method, thus confirming the structure of ketone A.

Ketone B which has an M^+ peak at m/z 522 in its mass spectrum showed $uv \lambda_{max}$ characteristic of a 2,4-dimethoxy benzoyl chromophore. The presence of a conjugated carbonyl (IR 1660 cm^{-1}) and of six methoxyl groups (δ 3.81, 3.83 and 3.85) and signals at 6.93 (s, 1H) and 7.83 (d, 2H, $J = 9.5$ Hz) led us to assign the structure 25. The structure was confirmed by an alternate synthesis involving acylation of 1,3-dimethoxybenzene with the diacid (26) in PPA (Kasturi and Damodaran 1969).

Cyclization of 3-(4-methoxyphenyl)-isovaleric acid using phosphorus pentachloride and aluminium chloride gave 6-methoxy-3,3-dimethylindan-1-one (27a). However, reaction of 3-(2,4-dimethoxyphenyl) propionic acid with phosphorus pentachloride followed by treatment of the resulting acid chloride with aluminium chloride in benzene did not give the expected indanone (27b), but gave two chloro ketones which have been formulated as 3-(2,4-dimethoxy-5-chlorophenyl) propiophenone (28) and 3-(2,4-dimethoxyphenyl-5-[1-keto-3-(2,4-dimethoxy-5-chlorophenyl) propyl]-propiophenone (29) on the basis of spectral data. Surprisingly, similar

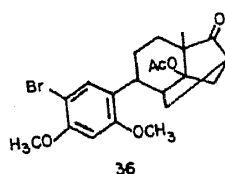
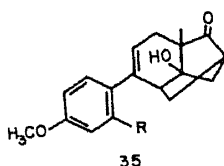
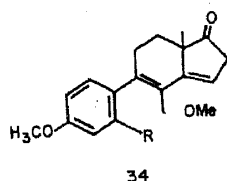
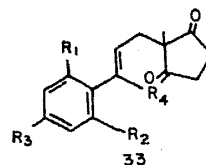
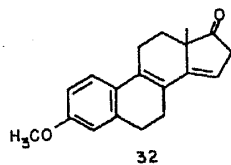
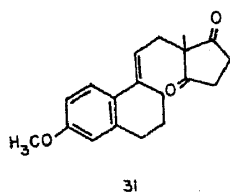


treatment of 3-(2,4-dimethoxyphenyl)-isovaleric acid gave chloro dihydrocoumarin derivative (30). Treatment of dimethoxybenzene derivatives with phosphorous pentachloride appears to be a general method for the preparation of monochloro dimethoxybenzene compounds (Kasturi and Abraham 1973).

2.6 Acid-catalysed cyclizations of *seco*-diones

Acid-catalysed cyclization of *seco*-dione (31) to the corresponding pentaenone (32) is an important step in the Torgov sequence for the total synthesis of steroids (Ananchenko and Torgov 1959, 1963). A variety of reagents have been used with success in this cyclization. We have tried similar cyclizations in a variety of *seco*diones, useful for the synthesis of B-*Seco*- and B-*nor* steroid analogs. (Kasturi *et al* 1982). The unusual types of compounds obtained in the cyclizations will be discussed further.

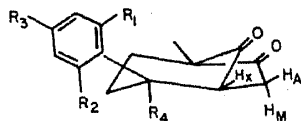
Attempts to effect the cyclodehydration of the *seco*-dione (33a) to the desired B-*seco*-pentaenone (34a) under different conditions failed. However, refluxing a solution of the *seco*-dione (33a) in 20% ethanolic hydrochloric acid for 1 hr gave a mixture of compounds from which a crystalline keto alcohol was isolated. On the basis of spectral data, this keto alcohol was assigned the tricyclodecane structure (35a). Acetylation of the keto alcohol followed by hydrogenation and bromination using dioxane dibromide gave the bromo compound (36), the structure of which was confirmed by x-ray crystal structure analysis (Kasturi *et al* 1972, 1974).



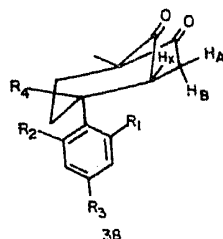
- a) $R_1 = R_3 = \text{OCH}_3$; $R_2 = \text{H}$; $R_4 = \text{C}_2\text{H}_4\text{OCH}_3$
 b) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{C}_2\text{H}_4\text{OCH}_3$
 c) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{CH}_3$
 d) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{CH}_2\text{CH}_3$
 e) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{Bu}^t$
 f) $R_1 = \text{OCH}_3$; $R_2 = R_3 = \text{H}$; $R_4 = \text{CH}_3$
 g) $R_1 = \text{OCH}_3$; $R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{CH}_3$
 h) $R_1 = \text{OCH}_3$; $R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{CH}_2\text{CH}_3$
 i) $R_1 = \text{OCH}_3$; $R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{vinyl}$
 j) $R_1 = \text{OCH}_3$; $R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{Bu}^t$
 k) $R_1 = \text{CH}_3$; $R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{CH}_3$
 l) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{H}$
 m) $R_1 = R_2 = \text{OCH}_3$; $R_3 = \text{H}$; $R_4 = \text{CH}_3$

Similarly, cyclization of the monomethoxy secondione (**33b**) under similar conditions produced the tricyclic keto alcohol (**35b**). The structure of the compound was evident from its spectral data which were similar to **35a** (Kasturi and Ramachandra 1975).

Acid-catalysed cyclization of seco-diones (**33a-l**) carried out with dry methanolic hydrogen chloride at room temperature resulted in the formation of a mixture of isomeric compounds. These could be separated by thin layer chromatography and were shown by spectral data to be the *exo*- and *endo*-bicyclo[3,2,1]-octane-6,8-diones (**37** and **38**). These isomeric diones exhibit characteristic line patterns for the oxomethylene and the bridgehead protons in their ^1H NMR spectra. Pattern 'A' (ABX): δ_A , δ_B 2.3–2.8 (m), δ_X 3.1–4 (m); Pattern 'B' (AMX): δ_A 2.4–2.7 (q, $J_{AX} = 8$ Hz, $J_{AM} = 20$ Hz) δ_M 2.8–3 (d, $J_{AM} = 20$ Hz), δ_X 3.3–4.1 (d, $J_{AX} = 8$ Hz). The isomers which exhibited pattern A were assigned the *exo*-2-aryl-*endo*-2-alkyl configuration (**37**) and those isomers which exhibited pattern B were assigned the *endo*-2-aryl-*exo*-2-alkyl configuration (**38**). These assignments were based (Kasturi *et al* 1980; Kasturi and Reddy 1981) on the expectation that the aryl group in the *endo* position as in **38** would deshield the *endo*-oxomethylene proton and thus lead to a larger chemical shift difference between *exo*- and *endo*-oxomethylene protons in this isomer. Similar shielding of the *endo*-oxomethylene proton by the *endo*-hydroxyl group in 2-hydroxy-2,5-dimethylbicyclo[3,2,1]octane-6,8-dione has been reported earlier (Hajos and Parish 1974). The spectral features of the bridgehead and the *oxo*-methylene proton signals of **37** and **38** did not agree for the configuration assigned (Kasturi *et al* 1981) and thus necessitated a reinvestigation of the previous assignments. To this end, we carried out the single-crystal x-ray structural analysis of the easily crystallisable isomer of 2-(2-methoxyphenyl)-2,5-dimethyl bicyclo[3,2,1]octane-6,8-dione which was previously assigned *endo* 2-methyl configuration (**37f**). X-ray analysis showed that the methyl group at C-2 and the bridge *oxo* group are *cis* with respect to each other, indicating an

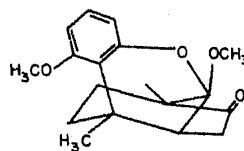


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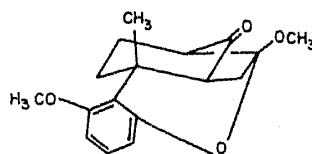


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- a) $R_1 = R_3 = \text{OCH}_3$; $R_2 = \text{C}_2\text{H}_4\text{OCH}_3$
 b) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{C}_2\text{H}_4\text{OCH}_3$
 c) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{CH}_3$
 d) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{CH}_2\text{CH}_3$
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 g) $R_1 = \text{OCH}_3$; $R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{CH}_3$
 h) $R_1 = R_3 = \text{OCH}_3$; $R_2 = \text{H}$; $R_4 = \text{CH}_2\text{CH}_3$
 i) $R_1 = R_3 = \text{OCH}_3$; $R_2 = \text{H}$; $R_4 = \text{vinyl}$
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 k) $R_1 = R_4 = \text{CH}_3$; $R_2 = \text{H}$; $R_3 = \text{OCH}_3$
 l) $R_1 = R_2 = \text{H}$; $R_3 = \text{OCH}_3$; $R_4 = \text{H}$
 m) $R_1 = R_2 = \text{OCH}_3$; $R_3 = \text{H}$; $R_4 = \text{CH}_3$



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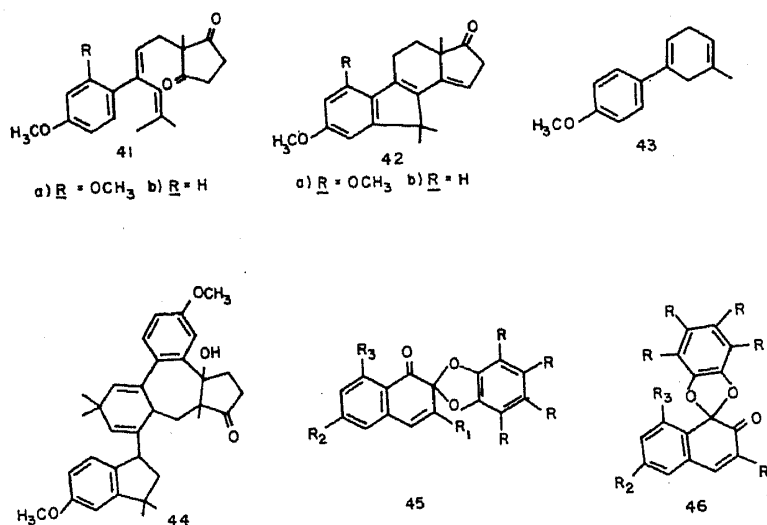


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exo-2-methyl-*endo*-2-(2-methoxyphenyl) configuration (38f) contrary to the assigned configuration (37f). Consequently, all the previous assignments had to be revised; the isomers which exhibited pattern A are now assigned the *endo*-2-aryl-*exo*-2-alkyl configuration and *vice-versa* (Kasturi *et al* 1981). ^1H and ^{13}C NMR of several bicyclo[3,2,1]octane diones have been discussed (Kasturi *et al* 1982).

Reaction of seco-dione (33m) with anhydrous methanolic hydrogenchloride gave 2-*endo*-(2,6-dimethoxyphenyl)-2-*exo*-methyl-5-methyl-bicyclo[3,2,1]octane-6,8-dione (38m) whose structure was confirmed by x-ray crystal structural analysis (Murthy *et al* 1982). No 2-*exo*-(2,6-dimethoxyphenyl)-2-*endo*-methyl bicyclo[3,2,1]octane dione (37m) was formed. Instead, another crystalline solid was isolated which showed a carbonyl frequency at 1740 cm^{-1} and in the NMR, two methyl singlets (δ 1.03 and 1.56), one aliphatic methoxy (3.32) and only one aromatic methoxy (3.79) group. On the basis of spectral data, two structures (39 and 40) were considered. NaBH_4 reduction of the solid gave a mixture of *endo*- and *exo*-alcohols which could be separated. On the basis of the PMR spectra of these alcohols especially the coupling constants, structure (39) was assigned to this solid. Probably, the *exo*-isomer (37m) formed in small quantities gave rise to this compound by a neighbouring group participation to release the excessive buttressing effect (Kasturi *et al* 1982).

Acid-catalysed (CH_2Cl_2 -conc. H_2SO_4) cyclization of the seco-dione (41a) gave the B-nor-steroid derivative (42a) in fairly good yield. However, cyclization of the desmethoxy seco-dione (41b) under similar conditions gave very little of the B-nor steroid derivative (42b), but gave two novel products. The structures of these two products, elucidated using their spectral data (PMR, CMR and mass) have been shown to be the simple cyclohexa-1,4-diene derivative (43) and the complex dibenz-azulene derivative (44). A probable mechanism has been suggested for the formation of these two novel products (Kasturi and Parvathi 1981).

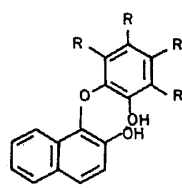
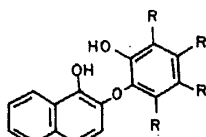
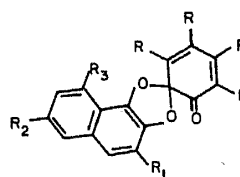
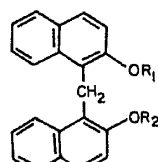
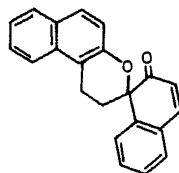


2.7 Oxidation with quinones

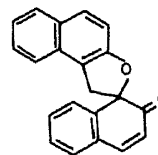
Both 1- and 2-naphthols undergo oxidative coupling with *O*-chloranil to give spirans (Kasturi *et al* 1970). While 1-naphthol gives the spiran (45a) on oxidation, 2-naphthol, unexpectedly affords a mixture of the two spirans (45a and 46a) indicating an unusual oxidative rearrangement. In order to study the generality as well as substituent effects on this novel rearrangement, a number of substituted 1- and 2-naphthols were synthesised (Kasturi and Sivaramakrishnan 1975, 1976) and their oxidative coupling reaction studied (Kasturi and Sivaramakrishnan 1978). It has also been shown that while oxydiphenols (47) undergo normal intramolecular oxidative coupling to give spirans (45) oxydiphenols (47a) undergo rearrangement to give a mixture of the spirans (45 and 46). The presence of chlorine atoms on the benzene ring is not necessary for this oxidative rearrangement as shown by oxidation studies with oxydiphenols (47b) (Kasturi and Ganesh Prasad 1983).

On the basis of this study, it was proposed that the oxidation of 2-naphthol derivatives could go through the formation of spiro-cyclohexadienone intermediate (49) which could open up in either direction to give the α - and β -spirans (45 and 46). The conformation of the phenoxy group, the oxidation potential of the quinone and the substrate (the naphtholic and the phenolic part in the oxydiphenols) along with steric and electronic effects of the substituents could explain the observed results (Kasturi and Ganesh Prasad 1983).

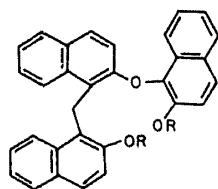
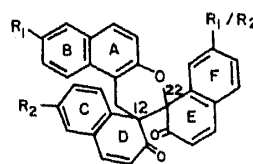
With a view to understand the reaction of *O*-chloranil with a substrate like *bis*-(2-hydroxy-1-naphthyl) methane (50a), the oxidation was carried out with different proportions of *O*-chloranil. Unexpectedly, spirans (45a & 46a), the dimer of 1,2-naphthoquinone -1-methide (51) along with the intramolecularly coupled product (52) were obtained (Kasturi *et al* 1979). When the reaction of 50a was carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene, an entirely new reaction occurred. The three products obtained were separated by careful column chromatography followed by thin layer chromatography. Two of them were identified as 51 and 52. The major compound obtained in this reaction had M^+ m/z 440 and gave a dihydro derivative (M^+ m/z 442) on hydrogenation. Structures 53a and 53b assigned to the

47
a) R = Cl b) R = H48
a) R = Cl b) R = H49
(R = Cl or H)50
a) R₁ = R₂ = H
b) R₁ = H; R₂ = CH₃

51

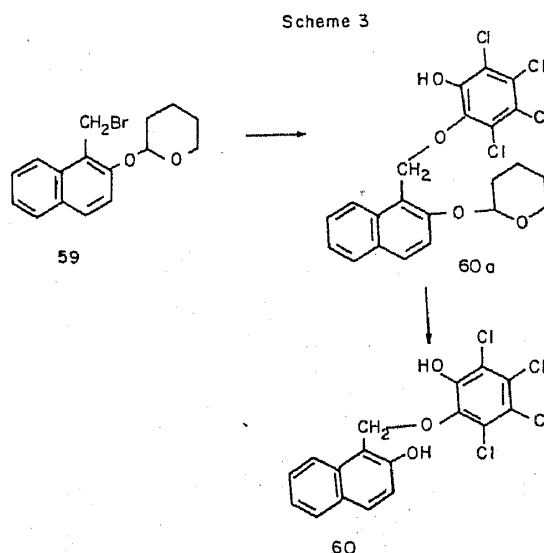
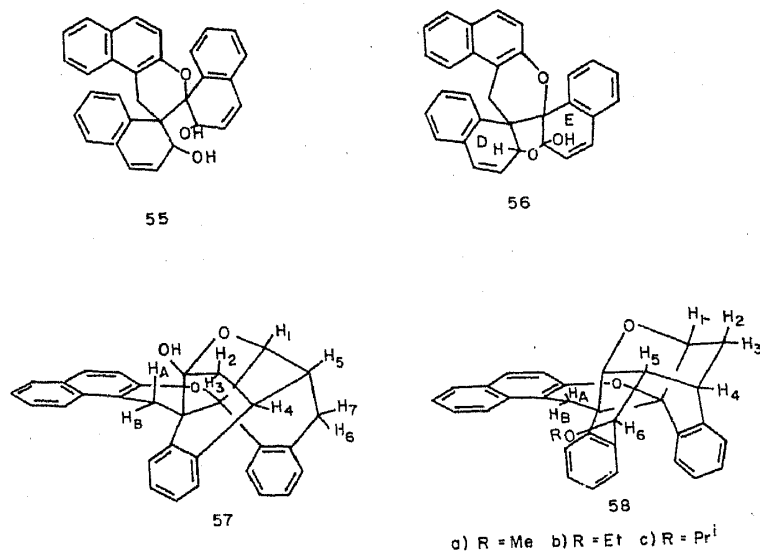


52

53
a) R = H b) R = CH₃54
a) R₁ = R₂ = H

dihydro and the corresponding dimethoxy compounds respectively from a study of their ^1H and ^{13}C NMR spectra were further corroborated by an unambiguous synthesis involving condensation of **50b** with 1-bromo-2-methoxy-naphthalene followed by demethylation with boron tribromide. On the basis of a detailed study of ^1H and ^{13}C NMR spectra, the unusual dispirodienone structure (**54**) was assigned to this compound. Results obtained from x-ray crystal structure analysis are in full agreement with this structure. It has been found that the $\text{C}_{12}\text{-C}_{22}$ bond is unusually long (1.616 Å) in this compound (**54**). A small amount of the *trans* product of **54** was also obtained in this oxidation (Kasturi *et al* 1984). Using this reaction, a series of bispironaphthalenones (**54**) (with different substituents (R_1 & R_2)) have been synthesised and a suitable mechanism suggested for its formation (Kasturi *et al* 1984).

With a view to preparing the biallylic alcohol (**55**) required for some studies of intramolecular (2+2) photocycloadditions (Kasturi *et al* 1981), the bispironaphthalenone (**54**) was reduced with sodium borohydride in THF. The biallylic alcohol (**55**) was obtained in only 15% yield. The major products of this reduction were the acetal (**56**) and the novel intramolecularly c-c coupled acetal (**57**). When the reduction was carried out with NaBH_4 in the presence of NaOH in aqueous THF, **56** was obtained with traces of **55** and **57**. However, reduction in MeOH-THF containing NaOH gave the novel methoxy c-c coupled acetal (**58a**) in good yield. Similarly, the ethoxy (**58b**) and the isopropoxy (**58c**) c-c coupled acetals were also prepared. The structures of all these compounds were established by ^1H and ^{13}C NMR spectral studies. The off-resonance decoupled ^{13}C NMR spectra of **57** shows three triplets and four doublets < 90 ppm, clearly indicative of intramolecular c-c coupling between the D & E rings. The occurrence of intramolecular c-c coupling **57** and **58** between benzylic and non-



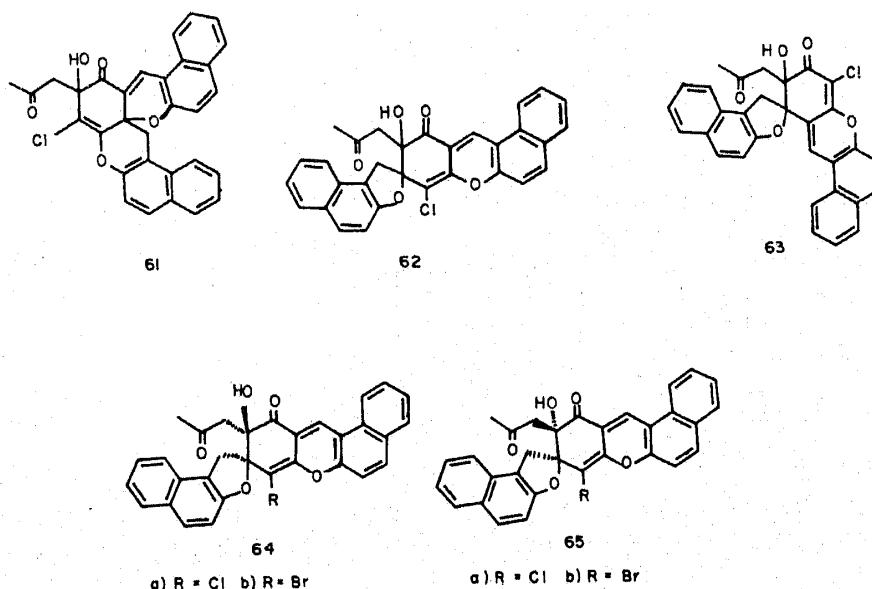
benzylic carbon atoms was established by their ^1H NMR spectra. Of the two alternative resulting structures, that with coupling between the D-ring benzylic carbon atom and the E-ring non-benzylic carbon atom was assigned to **57** on the basis of the OH resonances. There are significant differences in the ^1H NMR spectra of **57** and **58** in particular, the 1-H (*d* in **57**; *m* in **58**) and 2,3-H resonances (*dd* in **57**; AB '*q*' in **58**). The variation on the OH resonance position with the alkoxy group in **58** (R = CH₃, δ 5.33; R = Et, 5.43; R = Prⁱ, 5.50; cf **57**, 2.67) indicates that the hydroxy group is on the same side as the alkoxy group and probably hydrogen bonded to it (Kasturi and Raju 1982).

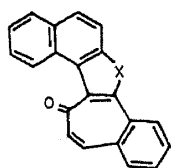
In connection with the oxidation studies, we needed the oxydiphenol (**60**). The synthesis of **60** was planned as indicated in scheme 3. The starting material (**59**) was prepared by NBS bromination of the pyranil ether of 1-methyl-2-naphthol. However, when the condensation of the bromo compound (**59**) with tetrachlorocatechol was carried out in refluxing acetone in the presence of anhydrous potassium carbonate, the

required compound (60a) was not formed. Instead, two isomeric compounds (M^+ 508) A and B and the dimer of 1,2-naphthoquinone-1-methide (51) were obtained. The presence of one chlorine atom was noticed in the mass spectrum of the isomeric compounds. The $^1\text{H NMR}$ spectra of the isomeric compounds exhibited two AB quartets, an OH signal (sharp in one case) and signals in the aromatic region. On the basis of the spectral data, 3 alternative structure (61, 62, 63) were considered, but structure (62) was considered more probable for compounds A & B. By a study of the $^{13}\text{C NMR}$ of these compounds in the presence of TAI reagent (Bose and Srinivasan 1975), it is now concluded that the two compounds A & B are diastereomers having structures (64a) and (65a). When the reaction was carried out with tetrabromocatechol instead of tetrachlorocatechol the corresponding isomeric monobromo compounds (64b and 65b) were isolated. Further confirmation of the structures by x-ray crystal structure studies is in progress (Kasturi *et al* 1983).

Oxidation of Abel's ketone (52a) with DDQ in dry benzene resulted in the formation of two products designated A and B, which show carbonyl absorption frequencies at 1628 and 1760 cm^{-1} respectively. Mass spectra (M^+ m/z 296) show that the two compounds are isomeric and are dehydrogenation products of 52. In $^1\text{H NMR}$ spectra, all the proton signals are in the aromatic region. On the basis of spectral analysis, a furanotropone structure (66) was assigned for compound A. The spectral properties are comparable to those of an isomeric furanotropone (67) reported in the literature (Chatterjee *et al* 1978). Further, the spectral properties of compound A and its dihydroderivative (68a) are similar to those of compounds (66b and 68b) reported by Dean and coworkers (Dean *et al* 1964). The tropone structure (66a) explains the presence of two deshielded one proton doublets at δ 8.64 and 9.6 in its NMR spectrum. X-ray crystal structure analysis of compound A confirmed its structure as 66a (Kasturi *et al* 1984).

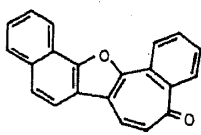
The high carbonyl frequency 1760 cm^{-1} of compound B implied the presence of a lactone moiety. On the basis of available spectral data of compound B and its transformation products (69 and 70), a tentative benzfulvene type of structure 71 has been assigned. Further work is in progress to confirm this structure.



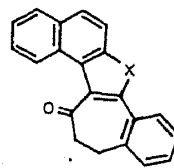


66

a) X = O b) X = NH

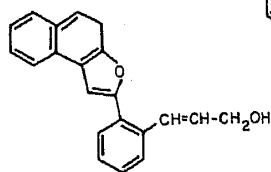


67

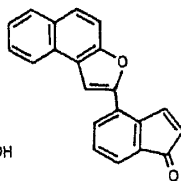


68

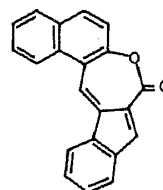
a) X = O b) X = NH



69



70



71

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