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Quinones and Related Compounds in Higher Plants. III.[1] Absolute Structure of Catalponol, a Naphthoquinone Congener of *Catalpa ovata*[2]

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Absolute structure of catalponol, a naphthoquinone congener of *Catalpa ovata* has been established as **1**.

Examination of the reaction of **1** and its oxidation product, catalponone (**2**) with BF_3 giving several derivatives including natural products such as 2,2-dimethylnaphthochroman (**12**), nordihydrolapachenole (**14**) and tetrahydrotectol (**15**), has offered interesting materials for considering the biosynthetic pathway of these substances.

In the preceding paper[1] we reported on the structure elucidation of six naphthoquinones isolated along with a congener designated as catalponol, the structure of which we describe in this paper.

Catalponol (**1**), $C_{15}H_{18}O_2$, $[\alpha]_D$ +11.0° (MeOH), is a colorless oil which shows infrared (IR) bands at 3450, 1680 and 1600 cm^{-1} and the ultraviolet (UV) absorptions at 248 and 291 nm. Its nuclear magnetic resonance (NMR) spectrum shows a multiplet of four aromatic protons in the region of δ 8.11—7.28, signals assignable to a proton on a hydroxy-bearing carbon and an olefinic proton around δ 5.36—4.81 and a pair of methyl singlets at δ 1.71 and 1.65. These spectral data suggest that compound **1** possesses a disubstituted benzene ring, one each of carbonyl and hydroxy group and presumably a *gem.* dimethyl group on a double bond.

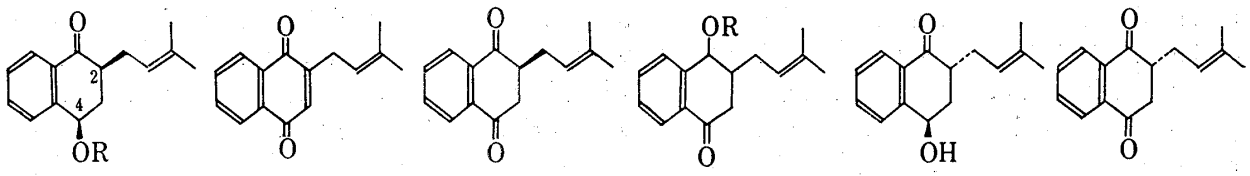
Manganese dioxide oxidation of **1** gave the product **2**, $C_{15}H_{14}O_2$, mp 57—58°, which was identified with the otherwise synthesized deoxylapachol.[4] Accordingly, it was clarified that **1** is a hydrogenated compound of **2**.

On the other hand, work up of **1** with Jones' reagent resulted in the oxidation of the hydroxy group yielding the corresponding diketo derivative **3**, $C_{15}H_{16}O_2$, mp 77—80°, $[\alpha]_D$ —75.4° (MeOH), which is designated as catalponone by taking into account its possible important biogenetic role. This compound shows neither any hydroxy absorption in IR nor any signal of a proton on a hydroxy-bearing carbon around δ 5.36—4.81 in NMR. There remains only an olefinic proton triplet at δ 5.13 (J=7 and 7 Hz).

Acetylation of **1** gave the monoacetate (**4**), $C_{17}H_{20}O_3$, the NMR spectrum of which shows a new signal of an acetoxy group at δ 2.20. Among the NMR signals of **1** around δ 5.36—4.81, one olefinic proton signal remains in the spectrum of this compound **4** at δ 5.15 as a deformed triplet and another one proton signal shifts downfield to δ 6.21 as a quartet (J=5 and 10 Hz).

These facts suggest that the acetoxy group of compound **4** would occupy secondary and equatorial position adjacent to a methylene group. Being compatible with the conclusion that **1** is a hydroderivative of deoxylapachol (**2**), this suggestion is further consistent with the supposition that the hydroxy group locates at the remoter benzylic position from the prenyl group. Accordingly, the planar structure of catalponol (**1**) was elucidated.

1) Part II: H. Inouye, T. Okuda, and T. Hayashi, *Chem. Pharm. Bull.* (Tokyo), **23**, 384 (1975).
2) Parts of this work have been published as preliminary communications; *Tetrahedron Letters*, **1971**, 3619.
3) Location: *Yoshida-shimoadachi-cho, Sakyo-ku, Kyoto*; *a*) Present address: *Faculty of Pharmaceutical Sciences of Kobegakuin University, Ikawaya-cho, Tarumi-ku, Kobe.*
4) W. Sandermann and M.H. Simatupang, *Chem. Ber.*, **96**, 2182 (1963).



1 : R=H
4 : R=Ac
7 : R=Bz

2

3

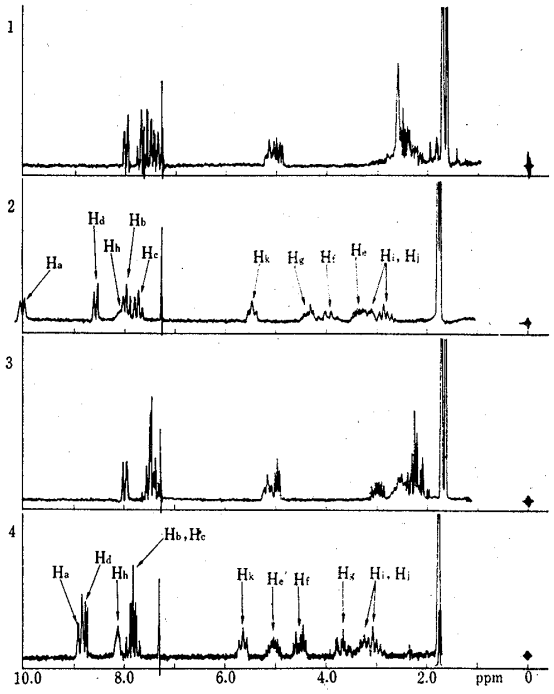
8 : R=H
9 : R=Ac

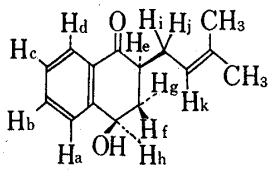
5

6

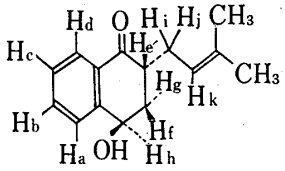
Bz=benzoyl

Chart 1





1



5

Fig. 1. 100 MHz NMR Spectra of Catalponol (**1**) and Epicatalponol (**5**)

1 catalponol (**1**)
2 catalponol (**1**) with $Eu(DPM)_3$ (0.17 mole equiv.)
3 epicatalponol (**5**)
4 epicatalponol (**5**) with $Eu(DPM)_3$ (0.18 mole equiv.)

Next, the relative configuration of the prenyl group and the hydroxy group of **1** was clarified with the aid of a 100 MHz NMR spectrum run in the presence of $Eu(DPM)_3$.

Even in the 100 MHz NMR spectrum of **1**, the assignment of the signals of methylene and methine protons in the region of δ 2.87—2.15 is difficult due to the overlapping of signals as shown in Fig. 1-1. Much less, the interpretation of the configuration of protons at both assymetric carbon is impossible. However, the use of Eu $(DPM)_3$ gave a first-order spectrum (Fig. 1-2) amenable to assign the signals. The shift reagent $Eu(DPM)_3$ has been known to associate more strongly with alcohols than with ketones,[5] causing larger paramagnetic shifts for protons locating closer to the hydroxy group. Thereby, under the influence of the shift reagent, signals become more deformed with decreasing distance between the proton and the hydroxy group.

It is thus inferred that the signal at δ 8.03 and the doublet at δ 10.01 could be due to Hh and Ha, respectively. The double doublet (J=8 and 1.5 Hz) at δ 8.56 is assigned to Hd from the coupling constants and the shift magnitude. Separate decoupling experiments

5) J.K.M. Sanders and D.H. Williams, *J. Am. Chem. Soc.*, **93**, 641 (1971).

revealed that among the two double triplets at δ 7.95 (J=8, 8 and 1.5 Hz) and δ 7.72 (J=8, 8 and 1 Hz), the former is coupled with Ha while the latter with Hd, leading to assign them to proton b and c. When the signal due to olefinic proton k at δ 5.46 was irradiated, the multiplet at δ 3.18 collapsed to a double doublet (J=14 and 3.5 Hz) and the quintet at δ 2.84 to a quartet (J=14 and 8 Hz) enabling us to assign the one to Hi and the other to Hj. Irradiation of proton h caused the collapse of the multiplet at δ 4.34 and the quartet at δ 3.94 to a double doublet (J=12 and 4 Hz) and a triplet (J=12 and 12 Hz), respectively, leading to assign the former to Hg and the latter to Hf. It is thus self-evident that the remaining multiplet at δ 3.36 is due to He. Assuming that three protons f, g and e form an ABX system, Jef, Jgf and Jeg should be 12, 12 and 4 Hz, respectively, requiring both protons e and f to occupy the trans diaxial position. We already mentioned that the acetoxy group of catalponol acetate (**4**) should assume an equatorial position. In the 100 MHz NMR spectrum of **1**, the quartet (J=12 and 4 Hz) of the proton h at δ 4.92 also clearly indicates that its hydroxy group occupies the equatorial position. It is thus concluded that the alicyclic ring of **1** assumes a half chair conformation, rendering the hydroxy group, the prenyl group and proton g equatorial, while proton e, f and h axial positions.

On treatment of **1** with dilute aqueous NaOH, the original material **1** and its isomer **5**, $C_{15}H_{18}O_2$, $[\alpha]_D$ +7.0° (MeOH) were obtained in a ratio of 7 to 3. **5** shows UV absorption maxima at 247 and 286 nm and IR bands at 3430, 1675 and 1600 cm^{-1}. In its 100 MHz NMR spectrum (Fig. 1-3), a multiplet of an olefinic proton k at δ 5.15 and a triplet (J=4 and 4 Hz) of proton h on a hydroxy-bearing carbon at δ 4.96 are observed along with signals due to four aromatic protons at δ 8.04—7.28 and a *gem.* dimethyl group at δ 1.70 and 1.62. Although the assignment of the remaining methine and methylene signals around δ 3.14—1.96 are difficult by the coincident position of the signals, they have been readily separated by the addition of $Eu(DPM)_3$ to allow facile assignment. Namely, the signal at δ 8.12 in Fig. 1-4 is due to proton h locating closest to the hydroxy group. Two double doublets at δ 8.87 and 8.79 are assignable to Ha and Hd, respectively. The multiplets around δ 7.96—7.68 region are attributable to protons b as well as c and the multiplet at δ 5.62 to proton k. Besides, multiplets at δ 5.04, 4.52 and 3.66 are due to protons e′, f and g, respectively, and those around δ 3.48—2.82 region to Hi and Hj. Splitting patterns of signals due to Hf and Hg show their J values being 5, 5 and 14 Hz as well as 4, 10 and 14 Hz, respectively. According to the double resonance experiments separately undertaken, irradiation of Hh caused the signal of Hf to collapse to a double doublet (J=14 and 5 Hz) while on irradiation of He′, the signal of Hg collapsed to a deformed doublet (J=14 Hz). Accordingly, considering the J values of the above-mentioned signals which are due to Hh, Hf and Hg of compound **5**, coupling constants Jhf, Jhg, Je′g, Jfg and Je′f should be 5, 4, 10, 14 and 5 Hz, respectively. These coupling constants indicate that the alicyclic ring of compound **5** assumes a half chair form causing the prenyl group, Hf and Hh to occupy equatorial positions, while the hydroxy group, Hg and He′ to assume axial positions. Thus the NMR data clearly reveal that **5** is an epimer of **1**, formed by the inversion of the configuration at C-2. This conclusion was substantiated by the fact that substance **6**, $C_{15}H_{16}O_2$, mp 77—80°, $[\alpha]_D$ +76.7° (MeOH), obtained by the Jones' oxidation of **5** is an antipode of **3**, an oxidation product of **1**. A considerably low yield of the epicatalponol (**5**) resulted on alkaline treatment of catalponol (**1**) compared with the amount of the recovered material (**1**) is also in accord with these conclusions derived from NMR data.

Considerations so far described completely clarified the relative configuration of catalponol (**1**). The absolute configuration of **1** was then inferred with the aid of the CD spectrum (in dioxane) of its benzoate (**7**), $C_{22}H_{22}O_3$, showing two Cotton effects at 243 ($\Delta\varepsilon$−6.3) and 228 nm ($\Delta\varepsilon$+7.9). The application of the dibenzoate chirality rule[6] leads to the conclusion that

6) N. Harada and K. Nakanishi, *Acc. Chem. Res.*, **5**, 257 (1972).

the C-4 of **1** has an *R* configuration as the sign of the first Cotton effect of **7** is negative indicating its chirality to be negative.

This conclusion is also compatible with the result of the application of Mills' rule.[7] Namely, the difference in the molecular rotation between catalponol benzoate (**7**) and catalponol (**1**) is (+51.3−25.3)=+26.0°.

Accordingly, the absolute structure of catalponol has been established as **1** and those of its derivative has been clarified.

In contrast to the manganese dioxide oxidation of **1** giving deoxylapachol (**2**), reduction of **2** with lithium aluminium hydride gave **1** as a racemate, which and whose acetate were identified with natural catalponol (**1**) and its acetate, respectively. Thus the structure of **1** was also established through the synthetic way. Reduction of **2** also afforded substance **8**, $C_{15}H_{18}O_2$, mp 52—54°, an isomer of **1**. The IR spectrum of **8** shows absorptions at 3400, 1675 and 1600 cm^{-1} indicating the presence of hydroxy and carbonyl groups as seen in **1**. Its NMR spectrum shows four aromatic proton signals around δ 8.11—7.30, a multiplet of one olefinic proton in the region of δ 5.35—4.91, a deformed doublet (J=6 Hz) at δ 4.70 attributable to a proton on a hydroxy-bearing carbon and two singlets at δ 1.73 and 1.61 due to a *gem.* dimethyl group. In the NMR spectrum of its acetate (**9**), $C_{17}H_{20}O_3$, the signal of the original alcoholic compound at δ 4.70 shifted remarkably downfield to δ 6.04 as a doublet whose J value is 6 Hz. If the hydroxy and the prenyl groups are *trans* to each other, they should assume equatorial positions giving a larger J value. Therefore, it is evident that both groups are on the adjacent carbons and also at *cis* positions.

Besides, in the course of the study on the structure of **1**, we treated **1** or **3** with BF_3 affording several naphthalene derivatives, on which we describe below briefly.

Reactions of **1** with BF_3 in Ac_2O gave two naphthalene derivatives **10**, $C_{17}H_{18}O_2$, mp 138—139° and **11**, $C_{19}H_{20}O_3$, mp 135—136°. The UV spectrum of **10** shows absorptions at 218, 245 and 338 nm. Its NMR spectrum shows multiplets of two aromatic protons at δ 9.00 and 8.28, a singlet of an aromatic proton at δ 7.80 and an AB type signal of two aromatic protons at δ 7.50. Two triplets (J=6.5 and 6.5 Hz) at δ 2.91 and 1.91 due to protons of two adjacent methylene groups, a singlet at δ 2.69 attributable to an acetyl group on an aromatic ring and a singlet at δ 1.45 due to a *gem.* dimethyl group are also observed in the spectrum.

Accordingly, this substance is thought to have structure **10** which is formed by the dehydration of the alicyclic ring of **1** accompanying aromatization and the successive etherization followed by the Friedel-Crafts reaction on the newly formed aromatic ring. Substance **11** has a similar UV spectrum to that of **10**. The NMR spectrum of **11** shows singlets of an acetyl group on an aromatic ring and an aliphatic acetyl group at δ 2.68 and 2.30, respectively, and an ABC multiplet at δ 3.50—2.75 attributable to three protons on the side chain. Two singlets of a *gem.* dimethyl group are observed at δ 1.61 and 1.36 revealing the nonequivalency of the methyl groups. Therefore, it has been clarified that this substance has an extra acetyl group on the side chain of **10** to be represented as **11**.

Treatment of **1** with BF_3 in benzene gave **12**, $C_{15}H_{16}O$, mp 35—36°, whose UV spectrum shows absorptions at 239, 300, 312 (sh.) and 327 nm. Its NMR spectrum shows signals around δ 8.33—7.03 due to six aromatic protons, a pair of triplets (J=6.5 and 6.5 Hz) at δ 2.87 and 1.87 due to two adjacent methylenes and a singlet at δ 1.40 attributable to a *gem.* dimethyl group. Thus, this substance has been deduced to be 2,2-dimethylnaphthochroman (**12**) which was isolated from teak[8] or several plants of the genus Galium.[9] The IR spectrum of this substance was identical with that of an authentic sample, which was described as an oil in the literature. The melting point of its picrate, 137—139°, is also identical with the literature value.

7) J.A. Mills, *J. Chem. Soc.*, **1952**, 4976.
8) W. Sandermann and M.H. Simatupang, *Naturwissenschaften*, **54**, 118 (1967).
9) A.R. Burnett and R.H. Thomson, *J. Chem. Soc.*, **1968**, 854.

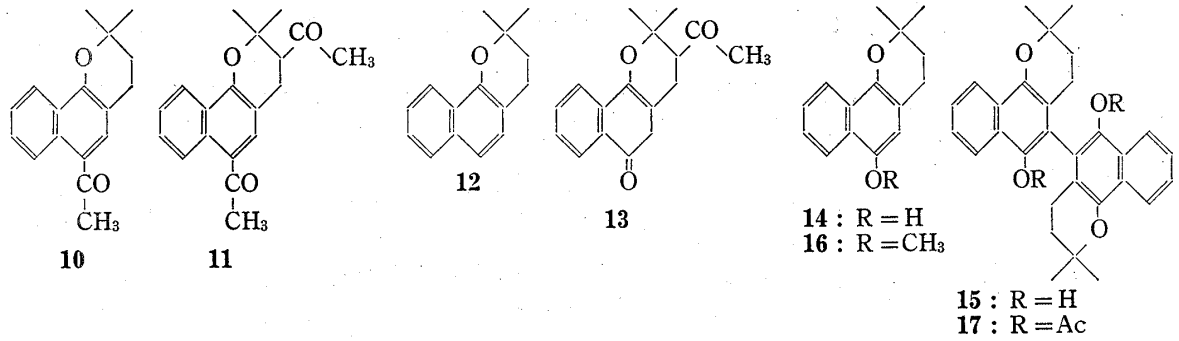


Chart 2

Work up of **3** with BF_3 in Ac_2O gave **13**, mp 103.5—105°. It shows UV absorptions at 249 and 304 nm, and IR bands at 1740, 1680 and 1600 cm^{-1}. Its NMR spectrum shows signals due to four aromatic protons around δ 8.13—7.11, signals attributable to five protons of methylene and methine in the region of δ 3.35—2.20, a singlet due to an aliphatic acetyl at δ 2.23, and a pair of broad singlets due to a *gem.* dimethyl group at δ 1.76 and 1.59. From these data, structure **13** is assigned to this substance.

Reaction of **3** with BF_3 in benzene in the dark gave **14**, $C_{15}H_{16}O_2$, mp 74—75°, while in the light it gave a mixture of **14** and **15**, $C_{30}H_{30}O_4$, mp 250—255° (decomp.). **14** was gradually converted into **15** in the light. The UV spectrum of **14** gives absorptions at 251, 329 and 341 nm and its NMR spectrum shows multiplets around δ 8.08 and 7.43 attributable to two each of aromatic protons and a singlet at δ 6.52 due to another aromatic proton. There appears also triplets at δ 2.78 and 1.84 attributable to two adjacent methylenes and a singlet of a *gem.* dimethyl group at δ 1.39. These findings suggested that this substance might be identical with nordihydrolapachenole[10] which has been isolated from the plant of the genus *Tabebuia.* However, as the substance **14** obtained in this experiment showed a considerably different melting point compared with the literature value,[10] it was converted into the methyl ether, which was found to be identical with an authentic sample of dihydrolapachenole (**16**).[11] The UV spectrum of **15** is similar to that of **14**. Its NMR spectrum shows signals due to eight aromatic protons at δ 8.40—7.34, a signal assignable to two hydroxy groups at δ 4.97, two pairs of methylene protons appearing as multiplet at δ 2.53—2.17 and a triplet at δ 1.79, respectively, and two *gem.* dimethyl groups appearing as a singlet at δ 1.40, while a singlet of an aromatic proton around δ 6.50 is lacking. These data revealed that this substance might be tetrahydrotectol which has been also isolated from the plant described above.[10,12] Actually, **15** was identified with an authentic sample of tetrahydrotectol by direct comparisons. Several properties of its acetate (**17**) were also identical with the literature values.

Facile chemical derivation of natural products such as **12**, **14** and **15** from catalponol (**1**) or its congener catalponone (**3**) now offers interesting material for considering the biogenesis of these substances. Works on the relevancy of substances **1**, **2** and **3** with biosynthesis of naphthoquinone derivatives are in progress.

Experimental[13]

Purification of Catalponol (1)——As the isolation procedure of **1** was precisely reported in the preceding paper, we here describe only its main properties. **1** is a colorless oil of bp 133—137° (bath temp., 0.13

10) A.R. Burnett and R.H. Thomson, *J. Chem. Soc.*, **1968**, 850.
11) Dihydrolapachenole employed for the comparison was obtained by the reduction of the authentic lapachenole (*cf.* W. Sandermann and H.H. Dietrichs, *Holz als Roh- und Werkstoff*, **15**, 24 (1957)). Later, we obtained dihydrolapachenole from Dr. R. Livingstone (Huddersfield) through Prof. R.H. Thomson.
12) W. Sandermann and M.H. Simatupang, *Chem. Ber.*, **97**, 588 (1964).
13) See footnote 9) in the preceding paper. NMR spectra of **1** and **5** were recorded on a Varian HA-100 spectrometer, and those of other compounds were measured on a Varian A-60 spectrometer in $CDCl_3$ with trimethyl silane (TMS) as an internal standard.

mmHg) and $[\alpha]_D^{34}$ +11.0° (c=1.2, MeOH). *Anal.* Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.75; H, 7.66, UV λ_{max}^{EtOH} nm(log ε): 248 (4.18), 291 (3.41).

Manganese Dioxide Oxidation of Catalponol (1)——To a solution of **1** (1 g) in benzene (100 ml) was added MnO_2 (10 g) and stirred at room temperature for 5.5 hr. After removal of the precipitates by filtration, the filtrate was concentrated *in vacuo*. The residue was chromatographed on silica gel (20 g, 2.1×13 cm) eluting with a mixture of benzene and AcOEt (9:1). The eluate was concentrated and the residue was recrystallized from petroleum ether to give 0.48 g of **2** as yellow needles, mp 57—58°, which were identified with an authentic sample of deoxylapachol (**2**) prepared from 1,4-dihydroxynaphthalene[4] by mixed melting point and comparisons of IR and NMR spectra. *Anal.* Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.52; H, 6.22. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660, 1610, 1590. UV λ_{max}^{EtOH} nm(log ε): 252 (4.29), 265 (sh.) (4.16), 331 (3.46). NMR δ: 8.23—7.63 (m, 4 arom. protons), 6.77 (t, J=1 and 1 Hz, >C=C<(CO, H)), 5.26 (deformed t, J=7.0 and 7.0 Hz, H>C=C<), 3.28 (difused d, J=7.0 Hz, $-CH_2-$), 1.80 and 1.68 (each s, $=C(CH_3)_2$).

Jones' Oxidation of Catalponol (1)——Jones' reagent[14] was added dropwise to a stirred solution of **1** (2.5 g) in acetone (25 ml) until the grayish green color of the reaction mixture turned into orange. The reaction mixture was immediately diluted with H_2O and extracted with $(C_2H_5)_2O$. The ethereal layer was dried over anhyd. $MgSO_4$ and the solvent was removed. Catalponone (**3**) was obtained as colorless needles from the methanolic solution of the residue. mp 77—80°. $[\alpha]_D^{29}$ −75.4° (c=1.0, MeOH). Yield 1.38 g. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.99; H, 6.97. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1595. UV λ_{max}^{EtOH} nm(log ε): 225 (4.56), 253 (4.10), 302 (3.48). NMR δ: 8.15—7.63 (m, 4 arom. protons), 1.70 and 1.60 (each s, $=C(CH_3)_2$).

Acetylcatalponol (4)——**1** (100 mg) was dissolved in pyridine (1 ml) and Ac_2O (1 ml) was added to the solution. After standing overnight, the reaction mixture was poured into ice water and extracted with $(C_2H_5)_2O$. The ethereal layer was washed with 5% HCl and H_2O successively and dried over anhyd. $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (20 g, 2.1×13 cm) eluted with CH_2Cl_2. After concentration of the eluate, the residue was further purified by vacuum distillation (bath temp., 124—128°, 0.05 mmHg) giving **4** as a colorless oil, yield 100 mg. *Anal.* Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.62; H, 7.42. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1685, 1600. UV λ_{max}^{EtOH} nm(log ε): 245 (4.16), 286 (3.33), 293 (sh.) (3.32). NMR δ: 8.20—7.94 (m, an arom. proton), 7.61—7.20 (m, 3 arom. protons), 6.21 (q, J=5 and 10 Hz, $-C\underline{H}OAc$), 5.15 (deformed t, J=7 and 7 Hz, H>C=C<), 2.20 (s, $-OCOCH_3$), 1.72 and 1.65 (each s, $=C(CH_3)_2$).

Epimerization of Catalponol (1)——To a solution of **1** (300 mg) in MeOH (3 ml) was added 1% aq. NaOH (1 ml) dropwise. The color of the reaction mixture changed from yellow to bluish purple. The mixture was immediately extracted with CH_2Cl_2 and the extract was washed with H_2O, dried over anhyd. $MgSO_4$ and the solvent was removed. The residue was chromatographed on silica gel (20 g, 1.6×21 cm) with $CHCl_3$ as eluent. At first, a colorless oil **1** (160 mg), and then its epimer **5** (71 mg) were eluted. Epicatalponol (**5**) was finally purified by distillation (bath temp., 133—137°, 0.12 mmHg) giving rise to a colorless oil. $[\alpha]_D^{33}$ +7.0° (c=0.57, MeOH). *Anal.* Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.97; H, 8.17. UV λ_{max}^{EtOH} nm(log ε): 247 (4.13), 286 (3.41).

Jones' Oxidation of Epicatalponol (5)——To a stirred solution of **5** (50 mg) in acetone (2 ml) was added dropwise Jones' reagent until the color of the reaction solution turned into orange. The mixture was immediately diluted with H_2O and extracted with $(C_2H_5)_2O$. The ethereal layer was dried over anhyd. $MgSO_4$ and the solvent was removed. The residue was chromatographed on silica gel (20 g, 1.6×20 cm) with $CHCl_3$ as eluent. Recrystallization from MeOH gave colorless needles, **6**, mp 77—80°. $[\alpha]_D^{24}$ +76.7° (c=0.50, MeOH). Yield 18 mg. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.67; H, 7.08. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1595. UV λ_{max}^{EtOH} nm(log ε): 225 (4.54), 253 (4.00), 302 (3.10). NMR δ: 8.23—7.68 (m, 4 arom. protons), 5.17 (difused t, J=7 and 7 Hz, H>C=C<), 1.70 and 1.60 (each s, $=C(CH_3)_2$).

Benzoyloxycatalponol (7)——To a solution of **1** (100 mg) in pyridine (2 ml) was added dropwise benzoyl chloride (200 mg). The reaction mixture was heated over a low flame until the crystals appeared were dissolved. After cooling, it was poured into ice water (10 ml) and extracted with $(C_2H_5)_2O$. After successive washing of the ethereal layer with 5% aq. $NaHCO_3$ and H_2O, it was dried over anhyd. $MgSO_4$ and the solvent was removed. The residue was chromatographed on silica gel (20 g, 2.1×13 cm) eluting with CH_2Cl_2 to give benzoate **7** as a colorless oil. Yield 45 mg. It was distilled under reduced pressure (bath temp., 152—155°, 0.06 mmHg). $[\alpha]_D^{36}$ +15.4° (c=1.2, MeOH). *Anal.* Calcd. for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.89; H, 6.61. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1705, 1680, 1600. UV λ_{max}^{EtOH} nm(log ε): 237 (4.35), 284 (3.37), 291 (sh.) (3.25). NMR δ: 8.26—7.36 (m, 9 arom. protons), 6.50 (q, J=5 and 10 Hz, $-C\underline{H}-OCOC_6H_5$), 5.50—5.00 (m, H>C=C<), 1.71 and 1.65 (each s, $=C(CH_3)_2$).

Reduction of Deoxylapachol (2) with $LiAlH_4$ and Acetylation of the Reduction Product——To a stirred

14) C. Djerassi, R.R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

solution of **2** (1.14 g) in abs. $(C_2H_5)_2O$ (40 ml) was added $LiAlH_4$ (195 mg). Therby, reddish purple precipitate developed in the reaction mixture. After 2 hr of stirring, a small amount of H_2O was added to the reaction solution and the precipitate was filtered off. The filtrate was dried over anhyd. $MgSO_4$ and the solvent was removed. The residue was chromatographed on silica gel (20 g, 2.1×13 cm) eluting with CH_2Cl_2. Fractions indicating a spot corresponding to that of catalponol (**1**) (*Rf* 0.49) on thin-layer chromatography (TLC) were combined and concentrated *in vacuo*. The residue was distilled under reduced pressure (bath temp., 132—135°, 0.05 mmHg) to give a colorless oil. Yield 79 mg. *Anal.* Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.01; H, 7.88. This substance was identical with catalponol (**1**) in IR, UV and NMR spectra together with TLC.

The racemic catalponol (**1**) (50 mg) was acetylated by the conventional method. Work up of the reaction mixture as in the case of optically active **1** gave racemic acetate as a colorless oil. Yield 33 mg. bp 127—135° (bath temp., 0.13 mmHg). Mass Spectrum *m/e*: 212 (M^+-CH_3COOH). The IR, UV and NMR spectra of this substance were superimposable with those of the acetate **4** of optically active natural catalponol (**1**).

Fractions of the above mentioned silica gel column chromatography eluted after racemic **1**, indicating the main spot at *Rf* 0.45 on TLC, were combined and concentrated *in vacuo* to give a colorless oil. Yield 306 mg. This substance was subjected to repeated preparative TLC and the band around *Rf* 0.45 was scratched and extracted with MeOH. After removal of the solvent, the residue was recrystallized from pet. ether giving rise to **8** as colorless prisms, mp 52—54°. Yield 9 mg. *Anal.* Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.70; H, 7.93. UV λ_{max}^{EtOH} nm(log ε): 250 (4.08), 293 (3.27).

Racemic **8** (100 mg) was acetylated by the usual method to afford 69 mg of crude acetate (**9**), which was recrystallized from EtOH yielding colorless prisms, mp 58—59°. Mass Spectrum *m/e*: 212 (M^+-CH_3COOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1683, 1600. UV λ_{max}^{EtOH} nm(log ε): 248 (4.06), 287 (3.21), 293 (sh.) (3.19). NMR δ: 8.18—7.93 (m, an arom. proton), 7.68—7.21 (m, 3 arom. protons), 6.04 (d, J=6 Hz, $-\underset{|}{C}\underline{H}OAc$), 5.10 (deformed t, J=7 and 7 Hz, $\underset{H}{}\rangle C{=}C\langle$), 1.71 and 1.48 (each s, $=C(CH_3)_2$).

Treatment of Catalponol (1) with BF_3 in Ac_2O——To a solution of **1** (230 mg) in Ac_2O (1 ml) was added 47% BF_3–$(C_2H_5)_2O$ (0.1 ml) and the mixture was left standing in a refrigerator overnight. After the addition of H_2O, the reaction mixture was extracted with $(C_2H_5)_2O$. The ethereal extract was dried over anhyd. $MgSO_4$ and the solvent was removed. The residue was chromatographed on silica gel (30 g, 2.1×24.5 cm) eluting with a mixture of benzene and AcOEt (95:5). Recrystallization of the fast eluted fractions from *n*-hexane gave **10** as colorless needles, mp 138—139°. Yield 77 mg. *Anal.* Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.01; H, 7.06. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665, 1625, 1575. UV λ_{max}^{EtOH} nm(log ε): 218 (4.19), 245 (4.55), 338 (4.02).

The residue obtained by concentration *in vacuo* of the slowly eluted fractions was dissolved in MeOH, treated with decolorizing carbon and then recrystallized from the same solvent giving 35 mg of **11** as colorless pillars, mp 135—136°. *Anal.* Calcd. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.88; H, 6.79. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715, 1665, 1625, 1570. UV λ_{max}^{EtOH} nm(log ε): 219 (4.32), 244 (4.57), 330 (4.06). NMR δ: 8.96 (m, an arom. proton), 8.26 (m, an arom. proton), 7.76 (s, an arom. proton), 7.71—7.33 (m, 2 arom. protons), 3.50—2.75 (m, $-CH_2\underline{C}\underline{H}-$), 3.05 (s, $-CH_2-$), 2.68 (s, arom. $COCH_3$), 2.30 (s, aliph. $COCH_3$), 1.61 and 1.36 (each s, $\underset{O}{}\rangle C(CH_3)_2$).

Treatment of Catalponol (1) with BF_3 in Benzene——To a solution of **1** (200 mg) in benzene (1 ml) was added 47% BF_3–$(C_2H_5)_2O$ (0.1 ml). After standing at room temperature for 2 hr, the reaction mixture was diluted with H_2O and extracted with $(C_2H_5)_2O$. The ethereal layer was dried over anhyd. $MgSO_4$ and the solvent was removed. The residue was chromatographed on silica gel (20 g, 1.9×17 cm) with $CHCl_3$ as eluent. After concentration of the eluate, the residue was recrystallized from MeOH to give colorless pillars, mp 35—36°. Yield 197 mg. *Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.09; H, 7.75. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635, 1600, 1575. UV λ_{max}^{EtOH} nm(log ε): 239 (4.57), 300 (3.85), 312 (sh.) (3.72), 327 (3.66). IR spectrum of this substance was identical with that of authentic 2,2-dimethylnaphthochroman (**12**).

Substance **12** thus obtained (70 mg) was mixed with a solution of picric acid (70 mg) in 95% aq. EtOH (0.6 ml) and heated to boiling. The solution was immediately cooled in ice water and the resulting reddish orange crystals were collected by filtration, washed with ice-cooled MeOH and recrystallized from MeOH to give reddish orange needles, mp 137—139°. Yield 117 mg. *Anal.* Calcd. for $C_{15}H_{16}O\cdot C_6H_3N_3O_7$: C, 57.14; H, 4.34; N, 9.52. Found: C, 57.24; H, 4.19; N, 9.58. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1625, 1600, 1560 (sh.), 1540. NMR δ: 8.18—7.97 (m, an arom. proton), 7.75—7.10 (m, 7 arom. protons), 2.85 (t, J=7 and 7 Hz, $-CH_2-$), 1.89 (t, J=7 and 7 Hz, $-CH_2-$), 1.40 (s, $=C(CH_3)_2$).

Treatment of Catalponone (3) with BF_3 in Ac_2O——To a solution of **3** (228 mg) in Ac_2O (1 ml) was added 47% BF_3–$(C_2H_5O)_2$ (0.1 ml). After standing at room temperature for 2 hr, the reaction mixture was diluted with ice water and extracted with $(C_2H_5)_2O$. The ethereal layer was washed with 5% $NaHCO_3$ and then with H_2O, and dried over anhyd. $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (30 g, 2.1×24.5 cm) eluting with a mixture of benzene and AcOEt (95:5). The eluate was concentrated and the residue was recrystallized from MeOH giving 144 mg of **13** as colorless pillars, mp

103.5—105°. *Anal.* Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.25; H, 6.56. UV λ_{max}^{EtOH} nm(log ε): 249 (4.06), 304 (3.26). NMR δ: 8.13—7.11 (m, 4 arom. protons), 3.35—2.20 (m, $-\overset{|}{\underset{|}{C}}H$ and $2\times-CH_2-$), 2.23 (s, $-COCH_3$), 1.76 and 1.59 (each broad s, $=C(CH_3)_2$).

Treatment of Catalponone (3) with BF_3 in Benzene——To a solution of **3** (115 mg) in benzene (1 ml) was added 47% BF_3–$(C_2H_5)_2O$ (0.1 ml). After standing for 2 hr, the reaction mixture was diluted with H_2O and extracted with $(C_2H_5)_2O$. The ethereal layer was dried over anhyd. $MgSO_4$ and the solvent was removed. The residue was chromatographed on silica gel (20 g, 1.9×17 cm) with CH_2Cl_2 as eluent. The fast eluted fractions giving a spot at *Rf* 0.71 on TLC were combined and concentrated. The residue was recrystallized from acetone giving tetrahydrotectol (**15**) as colorless prisms, mp 250—255° (decomp.). Yield 13 mg. *Anal.* Calcd. for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 78.98; H, 6.83. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 1630, 1590. UV λ_{max}^{EtOH} nm(log ε): 253 (4.89), 330 (4.08), 341 (4.13). NMR δ: 8.40—8.19 (m, 4 arom. protons), 7.73—7.34 (m, 4 arom. protons), 4.97 (s, 2×OH), 2.53—2.17 (m, $2\times-CH_2-$), 1.79 (t, J=6.0 and 6.0 Hz, $2\times-CH_2-$), 1.40 (s, $2\times=C(CH_3)_2$).

15 was identified with an authentic sample by comparisons of mp, IR and NMR spectra.

15 (10 mg) was acetylated by the usual method and the crude reaction product was recrystallized from acetone to give diacetyltetrahydrotectol (**17**) as colorless prisms, mp 253—254°. Yield 12 mg. *Anal.* Calcd. for $C_{34}H_{34}O_6$: C, 75.81; H, 6.36. Found: C, 75.52; H, 6.40. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1745, 1590, 1570. NMR δ: 8.43—8.20 (m, 2 arom. protons), 7.80—7.36 (m, 6 arom. protons), 2.38 (t, J=6.5 and 6.5 Hz, $2\times-CH_2-$), 1.95 (s, $2\times OCOCH_3$), 1.76 (t, J=6.5 and 6.5 Hz, $2\times-CH_2-$), 1.40 (s, $2\times=C(CH_3)_2$).

Fractions of the above described silica gel column chromatography eluted after **15**, showing a spot at *Rf* 0.53 on TLC were combined and concentrated. Recrystallization of the residue from pet. ether gave colorless needles of nordihydrolapachenole (**14**), mp 74—75°. Yield 42 mg. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.90; H, 7.26. IR ν_{max}^{Nujol} cm^{-1}: 3250, 1635, 1600. UV λ_{max}^{EtOH} nm(log ε): 251 (4.55), 329 (3.87), 341 (3.87). NMR δ: 8.27—7.90 (m, 2 arom. protons), 7.58—7.35 (m, 2 arom. protons), 6.52 (s, an arom. proton), 2.77 (t, J=6.5 and 6.5 Hz, $-CH_2-$), 1.84 (t, J=6.5 and 6.5 Hz, $-CH_2-$), 1.38 (s, $2\times-CH_3$).

When an ethereal solution of **14** was left standing in the light for 3 days, TLC examination of the solution revealed that all the starting material was converted into **15**.

To a solution of **3** (100 mg) in benzene (1 ml) was added 47% BF_3–$(C_2H_5)_2O$ (0.2 ml) in the dark and the mixture was allowed to stand for 30 min. After an addition of cracked ice, the reaction mixture was extracted with benzene and the extract was dried over anhyd. $MgSO_4$ and concentrated *in vacuo*. Recrystallization of the residue (106 mg) from pet. ether gave **14** as colorless needles, mp 74—75°. Yield 94 mg.

14 (20 mg) dissolved in a small amount of MeOH was mixed with CH_2N_2–$(C_2H_5)_2O$. After standing overnight, the reaction mixture was concentrated and the residue was subjected to repeated preparative TLC. The band around *Rf* 0.71 was scratched and extracted with benzene and the solvent was removed *in vacuo*. The residue was recrystallized from EtOH to give dihydrolapachenole (**16**) as colorless paltes, mp 75—77°. Yield 8 mg. Mass Spectrum *m/e*: 242 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1630, 1590. UV λ_{max}^{EtOH} nm (log ε): 249 (sh.) (4.46), 251 (4.48), 324 (3.83), 336 (3.82). NMR δ: 8.28—8.07 (m, 2 arom. protons), 7.60—7.35 (m, 2 arom. protons), 6.50 (s, an arom. proton), 3.94 (s, $-OCH_3$), 2.85 (t, J=7.0 and 7.0 Hz, $-CH_2-$), 1.88 (t, J=7.0 and 7.0 Hz, $-CH_2-$), 1.40 (s, $=C(CH_3)_2$).

This substance was identified with an authentic sample of **16** by mixed melting point and comparisons of IR and NMR spectra.

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