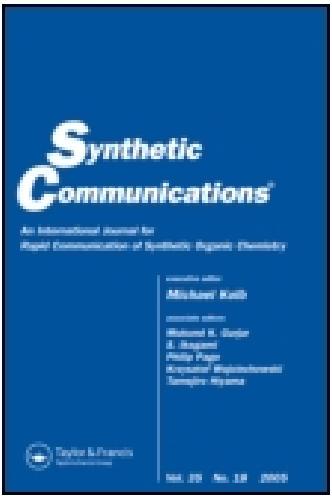


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Convenient Synthesis of Labdane and Drimane Analogues with o-Quinol Functionality

S. Meenakshi [a], A. Sivaramkrishnan [a], R. Padmakumar [a], Shreeshailkumar B. Hadimani [a] & Sujata V. Bhat [a]

[a] Department of Chemistry, Indian Institute of Technology, Powai, Mumbai, 400 076, India

Published online: 10 Jan 2011.

To cite this article: S. Meenakshi, A. Sivaramkrishnan, R. Padmakumar, Shreeshailkumar B. Hadimani & Sujata V. Bhat (2004) Convenient Synthesis of Labdane and Drimane Analogues with o-Quinol Functionality, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 34:22, 4065-4076, DOI: 10.1081/SCC-200036582

To link to this article: http://dx.doi.org/10.1081/SCC-200036582

SYNTHETIC COMMUNICATIONS®
Vol. 34, No. 22, pp. 4065–4076, 2004

Convenient Synthesis of Labdane and Drimane Analogues with *o*-Quinol Functionality

S. Meenakshi, A. Sivaramkrishnan, R. Padmakumar, Shreeshailkumar B. Hadimani, and Sujata V. Bhat*

Department of Chemistry, Indian Institute of Technology, Powai, Mumbai, India

ABSTRACT

The Diels–Alder reactions of 4-carbomethoxy-*o*-benzoquinone with substituted-1,3-dienes give high yields of the drimane and labdane analogues containing an orthoquinol moiety.

Key Words: Synthesis; Diels–Alder reaction; Labdane; Drimane Analogues; *o*-Quinol functionality.

*Correspondence: Sujata V. Bhat, Department of Chemistry, Indian Institute of Technology, Powai, Mumbai 400 076, India; Fax: 91(022) 2573480; E-mail: svbhat@chem.iitb.ac.in.

DOI: 10.1081/SCC-200036582 0039-7911 (Print); 1532-2432 (Online)

INTRODUCTION

There are many cyclic natural compounds with *o*-quinone moiety, which exhibit interesting biological activities (Fig. 1). For example, the eremophilane class of sesquiterpenes (**1**) displays phytotoxic properties.[1] Members of the quassinoid family (**2**) exhibit a gamut of biological activities, which include antimalarial, antitumor and anti-inflammatory activities.[2,3] Chinese drug Tanshen (*Salviae miltiorrhizae*) has been reported to have the effect of promoting blood circulation, removing blood stasis, and draining pus. A water-soluble derivative, sodium Tanshinone II-A sulfonate (**3**)[4] showed protective action against anorexia, ischaemia, and platelet aggregation in rats. In coronary patients, it reduced anginal pain and improved the ischemic changes in the electrocardiogram. Polyhydroxylated limonoid with decalin skeleton from neem[5] and drimanes from various plants display antifeedant activity.[6] The quinone methide, taxodione (**4**) from *Tadodium disticum*, has antitumor activity.[7]

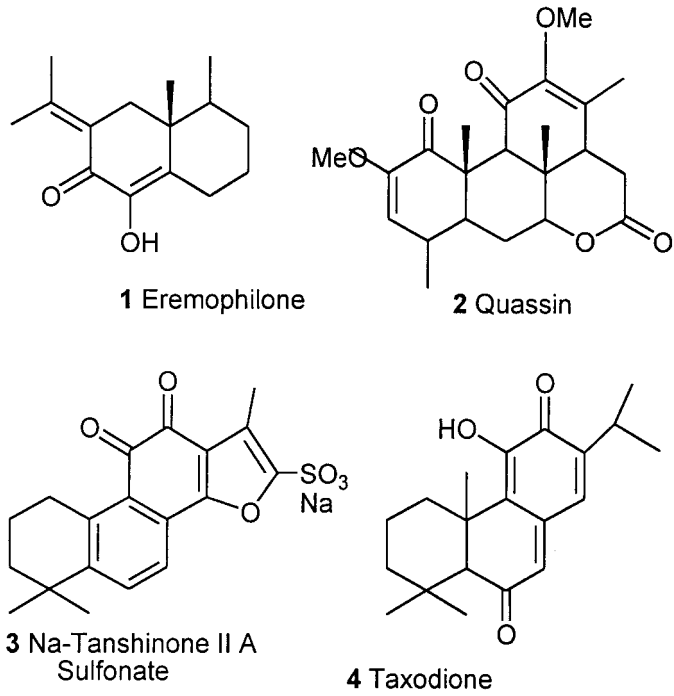


Figure 1. Examples of quinonoid natural products.

We report herein the reaction of 4-carbomethoxy-*o*-benzoquinone with substituted acyclic 1,3-butadienes to give high yields of drimane and labdane analogues[8] with *o*-quinol-A ring.

Orthoquinones are readily generated in situ by oxidation of catechols. The quinones, isolated in low yield by this procedure, are rather unstable to both light and water.[9] Orthoquinones exhibit properties of both diene and dienophile.[10,11] However, they had not received much attention as dienophiles, until the synthesis of tanshinones. Lee et al. had used the cycloaddition reaction of 3-methyl-4,5-benzofurandione, as the dienophile, with vinylcyclohexene, as the diene, promoted by ultrasound in the synthesis of tanshindiol A (Scheme 1).[12] Danishefsky et al. observed that the regioselectivity was influenced by the reaction solvent.[13]

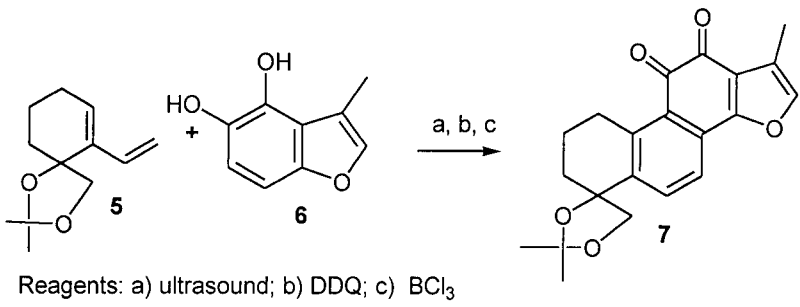
Ansell et al.[11] and Kraus and Taschner[14] had shown that *o*-quinones bearing an electron withdrawing substituent at 4-position are more reactive as dienophiles in cycloadditions with reactive acyclic dienes such as 2,3-dimethyl-butadiene and vinyl-cyclohexene respectively.

RESULTS AND DISCUSSION

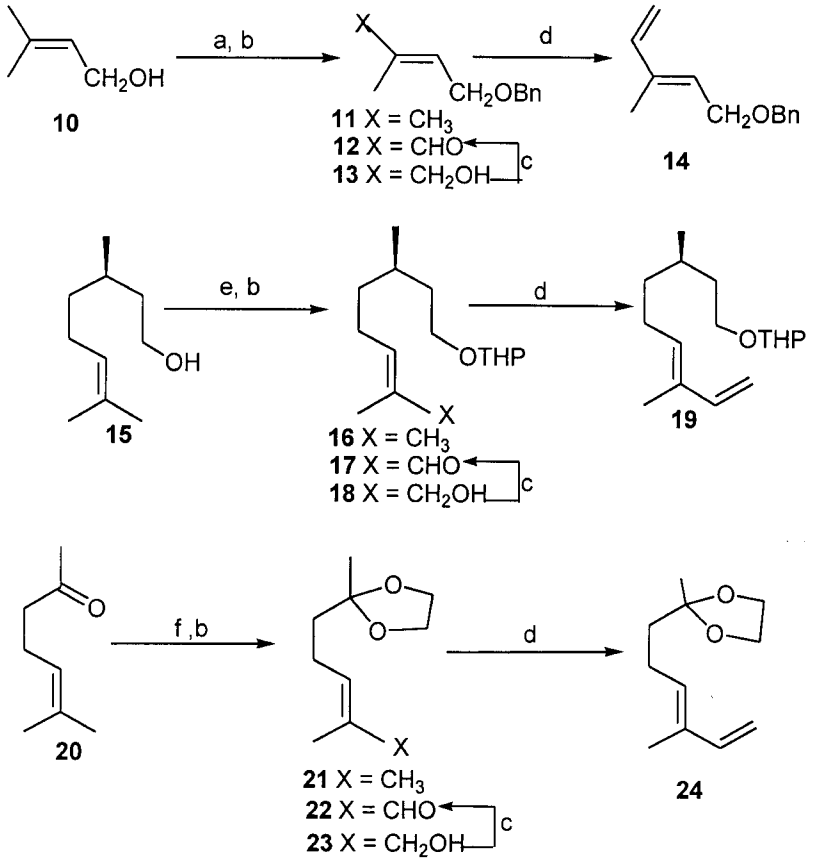
In continuation of the earlier work, we have studied the general application of the Diels–Alder reaction of 4-carbomethoxy-orthoquinones with acyclic 1- and/or 2-substituted-1,3-butadienes.

The 1.3-dienes **14**, **19**, and **24** were prepared from 3-methyl-2-butenol, 3,7-dimethyl-6-octenol (citronellol) and methylheptenone, respectively, in three steps (Scheme 2).

For the synthesis of diene **14**, 3-methyl-2-butenol (**10**) was first protected as the benzyl ether (**11**) and was subjected to a modified Sharpless oxidation[15] by using SeO_2/TBHP in dichloromethane, which oxidizes the



Scheme 1. Synthesis of tanshinone skeleton through Diels–Alder reaction.



Reagents: a) NaH, $C_6H_5CH_2Br$; b) SeO_2, TBHP, CH_2Cl_2; c) Pyridinium dichromate, CH_2Cl_2; d) $Ph_3P^+CH_2I^-$ + BuLi; e) DHP, ceric ammonium nitrate; f) Ethylene glycol, H^+

Scheme 2. Synthesis of 1,2-disubstituted 1,3-dienes.

trans-methyl group to aldehyde **12**. This compound was identified by the disappearance of the methyl group and the appearance of peak at δ 9.4 in the ^{1}H NMR and the appearance of signal at 1705 cm^{-1} for the C=O stretching in the IR spectrum. The allylic alcohol **13**, which was obtained as the coproduct in this reaction, was oxidized to the required aldehyde. The aldehyde **12** was treated with a Wittig reagent (methyl triphenylphosphonium iodide

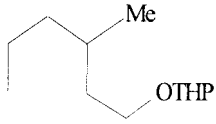
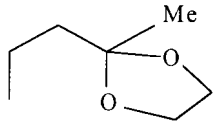
and n-BuLi) to give the required conjugated diene **14**. The dienes **19** and **24** were similarly prepared by starting from citronellol (**15**) and methyl heptenone (**20**), respectively.

The Diels–Alder reactions of 1,2-disubstituted-1,3-dienes (**8**, **9**, **14**, **19**, and **24**) and 4-carbomethoxy-*o*-benzoquinone (**25**) were carried out at 0°C room temperature for the time mentioned in Table 1 (Scheme 3). The reaction was performed in a solvent mixture of benzene-diethyl ether (3 : 1) in the absence of light. The products, substituted 1-hydroxy-2-oxo-5,8-dihydro-4a-hydronaphthalenes (**26–30**) were characterized by MS, UV, IR, and NMR spectra.

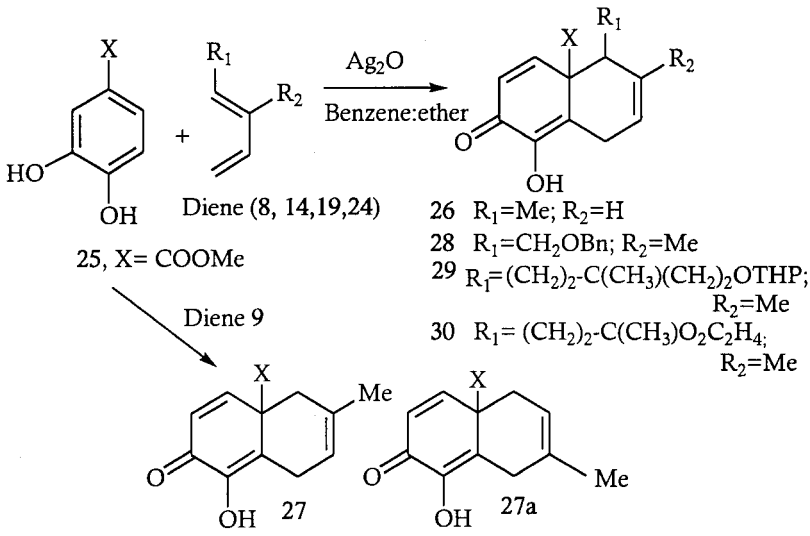
o-Quinones, being unstable, are prone to rapid dimerization.[12] To circumvent this problem and to increase yield of the cycloaddition reaction, generally, the reactions were carried out at 0°C room temperature in the absence of light.

The regioselectivity of cycloaddition in the reactions of unsymmetrically substituted dienes determines the subsequent synthetic use of the cycloadduct formed. In the cycloaddition between the unsymmetrical dienes and dienophile, a possibility exists of forming at least two regioisomers.[16] All dienes substituted at C-1 gave endo adducts as the sole product (Scheme 3). This was based on spectral analysis. The IR spectra of cycloadducts showed bands in the regions 3500, 1740, and 1680 cm^{-1}, indicating the presence of hydroxyl, ester, and conjugated carbonyl groups. The ^1H NMR spectra of

Table 1. Diels–Alder adducts of 1,3-dienes with 4-carbomethoxy-orthobenzoquinones.

Diene	R_1	R_2	Time (hr)	Adduct (Yield %)
8	Me	H	0.5	**26** (85)
9	H	Me	0.5	**27** (80)[a]
14		Me	3.0	**28** (75)
19		Me	3.0	**29** (75)
24		Me	8.0	**30** (85)

[a]Contains regioisomer **27a** in almost equal amount.



Scheme 3. Diels–Alder reaction of 1,3-dienes with 4-carbomethoxy-orthobenzoquinones.

the adducts showed a pair of doublets (1H each), around δ 6.5 and δ 6.9, with coupling constant of around 9.9 Hz, assigned for ring-A 3-H and 4-H protons, respectively, and a D_2O exchangeable signal due to –OH group. The 6-H and 7-H olefinic protons resonate as a pair of multiplets around δ 5.7 and 5.9. Thus, the product was formed through Diels–Alder reaction followed by enolization of the resulting α-diketone to the tautomeric diosphenol. This was confirmed not only by the high-resolution ^{1}H NMR spectrum but also by acetylation of the enol hydroxy group. The formation of the enol acetate was confirmed by the ^{1}H NMR spectrum of the acetate (additional singlet at δ 2.3, 3H) and IR spectrum (additional signal at 1728 cm^{-1}). The regioselectivity of adducts was further supported by NMR, NOESY experiment on adduct **26**, which showed connectivity between carbomethoxy and methyl groups.

No dimerization products of *o*-quinones were observed. Unlike earlier reports, neither bis adduct[17] nor benzodioxane adduct[18] were observed under the present reaction conditions.

CONCLUSIONS

Thus, the reaction of 4-carbomethoxybenzoquinone with substituted 1,3-butadienes gave drimane and labdane analogues with *o*-quinol-A ring.

Various functionalities, such as α,β-unsaturated ketone, ester, trisubstituted olefin, etc., can be exploited further in the synthesis of various analogues of bioactive terpene natural products. The method, in general, which is carried at ambient conditions with high yields of adducts, has the potential for rapid assembly of decalin skeleton with an *o*-quinone moiety and can be further exploited for synthesis of several analogues.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer model 681 spectrometer. ^{1}H NMR and ^{13}C NMR, spectra were recorded on 300 MHz and 125 MHz spectrometers in $CDCl_3$ with TMS as internal standard. Microanalysis was done on Carlo Erba Strumentazinone 1106 elemental analyzer. Silica gel (100–200 mesh) used for column chromatography was activated by heating at 120°C for 4 hr. Dienes **8** and **9** were obtained from Aldrich. Diene **24** was obtained as described earlier.[19]

Synthesis of diene 14

Synthesis of 3-Methyl-2-buten-1-ol Benzyl Ether (**11**)

NaH (50% suspension in oil, 5.28 g, 110 mmol), taken in a flame-dried three-necked, round-bottomed flask fitted with an addition funnel and a reflux condenser, was washed with dry petroleum ether. Dry THF (35 mL) was added to the flask and cooled to 0°C. 3-Methyl-2-butenol (**10**, 7.95 g, 92.5 mmol) in THF (50 mL) was taken in the addition funnel and added dropwise to the suspension of NaH in THF. The reaction mixture was allowed to reflux for an hour, cooled again to 0°C, and a mixture benzyl bromide (18.8 g, 110 mmol) in dry THF (50 mL) was added to the reaction mixture via a syringe. The reaction mixture was stirred at the same temperature for an hour and then refluxed for 3 hr. It was then quenched with water, THF evaporated in vacuo and extracted with ethyl acetate, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the mixture was purified over silica gel column to obtain the 3-methyl-butenyl-benzyl ether (**11**, 13.98 g, 86%).

Oxidation of 3-Methylbutenyl Benzyl Ether (**11**)

SeO_2 (2.28 g, 20.6 mmol), 70% aq. tert-butylhydropetoxide (TBHP, 20.5 mL, 160 mmol) in dichloromethane were stirred for 30 min at room

temperature. To the reaction mixture, the 3-methylbutenyl benzyl ether (**11**, 13.2 g, 75 mmol) was added and stirred for 6 hr. Stirring was further continued for 16 hr. Reaction mixture was quenched with 10% sodium bisulfite solution, extracted with dichloromethane, washed with $NaHCO_3$, water, and brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and column performed over silica gel to obtain the aldehyde **12** (7.84 g, 55%) and the allylic alcohol **13** (2.74 g, 19%).

Wittig Reaction of the Aldehyde **12**

Methyltriphenylphosphonium iodide (10.38 g, 25 mmol) was taken in a flame-dried three-necked flask under nitrogen atmosphere in dry THF (50 mL). The reaction mixture was cooled to 0°C and n-BuLi (1.6 M in hexane, 15.6 mL, 25 mmol) was added dropwise via syringe, and the reaction was allowed to stir for 30 min at room temperature. The reaction mixture was cooled to 0°C again, and a solution of the aldehyde **12** (3.85 g, 20 mmol) in dry THF (10 mL) was added dropwise through syringe and allowed to stir for 3 hr. Reaction quenched with a slow addition of saturated NH_4Cl solution, THF evaporated in vacuum, and the residue was extracted with ethyl acetate, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the residue was purified over silica gel column to give the 1,3-diene **14** (3.24 g, 86.2%).

IR (Neat, ν_{max}): 3032, 2927, 2868, 1617, 1522, 1459, and 1374 cm^{-1}.

Synthesis of 1,3-diene 19

Tetrahydropyranyl Ether of Citronellol (**16**)

Citronellol (**15**, 8 g, 51.2 mmol) was added to a solution of dihydropyran (5.04 g, 60 mmol), ceric ammonium nitrate (catalytic amount) and acetonitrile (80 mL) at 10°C with stirring.[20] The stirring was continued for an hour at room temperature. After the reaction was completed, the solvent was removed in vacuum, the residue was extracted with ether, washed with brine, dried over anhydrous Na_2SO_4, and solvent was removed in vacuum. The residue was subjected to column chromatography over silica gel to give the citronellolyl-tetrahydropyran ether (**16**, 10.22 g, 85%).

Oxidation of Citronellolyl-tetrahydropyran Ether (**16**)

Selenium dioxide (0.998 g, 9 mmol), 70% *tert*-butyl hydroperoxide (9 mL, 70 mmol) were stirred in dry dichloromethane (35 mL) for 30 min.

To this, a solution of the citronellolyl-tetrahydropyran ether (**16**, 8.4 g, 35 mmol) in dry dichloromethane (40 mL) was added and allowed to stir for 16 hr at room temperature. After the reaction was completed, the mixture was quenched with 10% sodium bisulfite solution, extracted with dichloromethane. The organic layer was then washed with $NaHCO_3$, water, and brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuum, and column chromatography was performed over silica gel to obtain the aldehyde **17** (3.17 g, 36%) and the alcohol **18** (2.96 g, 33%).

Aldehyde **17**: IR (Neat, ν_{max}): 3028, 2917, 1692, 1594, 1459, and 1374 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 9.6 (1H, s), 6.6 (1H, t), 4.5 (1H, m), 4.1–3.4 (4H, m), 2.2 (2H, m), 2.1 (3H, s), 1.7–1.3 (11H, m) and 0.95 (3H, d).

Wittig Reaction of Aldehyde **17**

Methyltriphenylphosphonium iodide (4.14 g, 10 mmol) was taken in a three-necked round-bottomed flask containing dry THF (30 mL). The flask was cooled to 0°C and to this was added n-BuLi (1.6 M in hexane, 6.6 mL, 10 mmol) in drops via syringe. The reaction mixture stirred at room temperature for 30 minutes, cooled again to 0°C and a solution of the aldehyde **17** (2.0 g, 7.87 mmol) in 10 ml of dry THF was added via syringe. Reaction was allowed to stir for 3 h at room temperature and quenched with saturated NH_4Cl. THF was evaporated *in vacuum* and the residue was extracted with ethyl acetate, ethyl acetate extracts were washed with brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the column chromatography of the residue over silica gel using pet ether: ethyl acetate as eluent gave 1,3-diene **19** (1.6 g, 81% yield).

IR (Neat, ν_{max}): 2949, 2868, 1613, 1609, 1464 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 6.2 (1H, m), 5.3 (1H, m), 5.0 (2H, m), 4.5 (1H, m), 4.0–3.4 (4H, m), 1.9–1.6 (5H, m), 1.6–1.4 (11H, m), and 0.95 (3H, d).

General Procedure for the Diels–Alder Reaction of 4-Carbomethoxybenzoquinone with 1,3-Dienes

To a solution of methyl 3,4-dihydoxy-benzoate (**25**, 1.5 mmol), 1,3-diene (**8**, **9**, **14**, **19** or **24**, 1 mmol) cooled to 0°C in benzene: ether (3 : 1), was added freshly prepared Ag_2O (2.0 mmol) and stirring continued for 3 hr at 0°C and then at room temperature for the period mentioned in Table 1. The reaction mixture was filtered through celite, washed with ether, the filtrates were combined, dried and evaporated. The column chromatography of the residue over silica gel gave the products **26–30** in the yields mentioned in Table 1.

Spectral data of the adducts, 26–30

5,8-Dihydro-1-hydroxy-4a-methoxycarbonyl-5-methyl-naphthalen-2-(4a*H*)-one (**26**)

IR (Neat, ν_{max}): 3450, 1740, and 1680 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.9 (1H, d, J 9.88), 6.56 (1H, d, J 9.88), 5.84 (1H, m), 5.68 (1H, dt, J 13.2, 4.4), 3.7 (3H, s), 3.42 (1H, m), 3.3 (1H, m), 3.04 (1H, m), 1.78(1H, bs), 0.77(3H, d, J = 7 Hz); MS: m/z 234 (M^+); Analysis: $C_{13}H_{14}O_4$ requires: C, 66.66%; H, 6.02%; Found C, 66.40%, H, 5.81%.

5,8-Dihydro-1-hydroxy-4a-methoxycarbonyl-6 (or 7)-methyl-naphthalen-2-(4a*H*)-one (**27** and **27a**)

IR (Neat, ν_{max}): 3400, 1740, and 1680 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.97 and 6.93 (1H, d, J = 9.9), 6.5 and 6.46 (1H, d, J = 9.9), 5.45 (1H, m), 3.68 and 3.67 (3H, s), 3.48 (2H, d, J_{gem} = 21.8), 3.1–3.0 (2H, m), 2.05 (1H, m), 1.8 (3H, s); MS: m/z 234 (M^+).

5-(Benzyloxymethyl)-5.8-Dihydro-1-hydroxy-4a-methoxycarbonyl-6-methyl-naphthalen-2-(4a*H*)-one (**28**)

IR (Neat, ν_{max}): 3490, 1750, and 1670 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.33 (5H, m), 7.0 (1H, d, J = 9.7), 6.62 (1H, brs), 6.46 (1H, d, J = 9.7), 5.43 (1H, m), 4.32 (2H, m), 3.60 (3H, s), 3.31 (3H, m), 3.05 (2H, m), 1.78 (3H, s); MS: m/z 340 (M^+); Analysis: $C_{20}H_{22}O_5$ requires: C, 71.17%; H, 6.26%; Found: C, 70.81%; H, 6.26%.

5,8-Dihydro-1-hydroxy-4a-methoxycarbonyl-6-methyl-5-(3′-methyl-5′-tetrahydro-pyranyloxy-pentan-1′-yl)-naphthalen-2(4a*H*)-one (**29**)

IR (Neat, ν_{max}): 3400, 1730, and 1650 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.9 (1H, d, J = 9.9), 6.5 (1H, d, J = 9.9), 5.4 (1H, m), 4.8 (1H, brs,-O-CH-O-), 3.8 (3H, m), 3.65 (3H, s), 3.4 (2H, m), 3.0 (2H, m), 1.8 (3H, s), 1.9–1.4 (14H, m), 0.8 (3H, d, J = 6.6); MS: m/z 418 (M^+); Analysis: $C_{24}H_{34}O_6$ requires: C, 68.87%, H, 8.18%; Found: C, 68.64%; H, 8.25%.

5,8-Dihydro-1-hydroxy-4a-methoxycarbonyl-6-methyl-5-(3′-methylenedioxy-butan-1′yl)-naphthalen-2-(4a*H*)-one (**30**)

IR (Neat, ν_{max}): 3400, 1740, and 1650 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.9 (1H, d, J = 9.8), 6.6 (1H, brs,-OH), 6.5 (1H, d, J = 9.8), 5.4 (1H, m), 3.8

(4H, m), 3.6 (3H, s), 3.3 (1H, m), 3.0 (1H, m), 2.9 (1H, m), 1.8 (3H, s), 1.6 (2H, m), 1.16 (2H, m), 1.1 (3H, s); MS: m/z 348 (M^+); Anal. $C_{19}H_{24}O_6$ requires: C, 65.50%; H, 6.94%; Found: C, 65.38%; H, 6.75%.

ACKNOWLEDGMENTS

The spectral assistance from R. S. I. C., Bombay and T. I. F. R. Mumbai and sample of citronellol from S. H. Kelkar and Co., Mumbai are gratefully acknowledged. We are thankful to Council of Scientific and Industrial Research for financial assistance.

REFERENCES

1. Kenfield, D.; Bunkers, G.; Strobel, G.; Sugawara, F. *Phytotoxins and Plant Pathogenesis*; Graniti, A., Durbin, R.D., Ballio, A., Eds.; Springer-Verlag: Berlin, Heidelberg, 1989; 319.
2. Kupchan, S.M.; Britton, R.W.; Lacadie, J.A.; Ziegler, M.F.; Sigel, C.W. The isolation and structural elucidation of brucianin and brucantitriol, new potent antileukemic quassinoids from Brucea antidysenterica. J. Org. Chem. **1975**, *40*, 648.
3. Hall, I.H.; Lee, K.H.; Imakura, Y.; Okano, M.; Johnson, A. Antiinflammatory agents III, structure-activity relationships of Brusatol and related quassinoids. J. Pharm. Sci. **1983**, *72*, 1282.
4. Lee, J.; Snyder, J.K. Ultrasound promoted Diels–Alder reactions-synthesis of tanshinone II, nortanshinone and ($\pm$) tanshinone-B. J. Am. Chem. Soc. **1989**, *111*, 1522.
5. Govindachari, T.R. Chemical and biological investigation on *Azadirachta indica* (the neem tree). Curr. Sci. **1992**, *63*, 117.
6. Bhat, S.V. Bioactive terpenoids. Life Chemistry Rep **1994**, *12*, 137.
7. Kupchan, S.M.; Karim, A.; Morks, C. Isolation, structure elucidation and antitumour activity of Taxodone and taxodione. J. Am. Chem. Soc. **1968**, *90*, 5923.
8. Tsichritzis, F.; Jakupovic, J. Diterpenoids of *Leyssera gnapheloides*. Phytochemistry **1991**, *30*, 211.
9. Bruce, J.M.; Creed, D. Light induced and related reactions of quinines part IV, reactions of some quinines carrying formyl group. J. Chem. Soc.(C). **1970**, 649.
10. Kloetzel, M.C.; Dayton, R.P.; Abadir, B.Y. Synthetic analogues of cortical hormone, homogentisic acid and 2,2,5-trihydroxyacetophenone

derivatives from hydroxyacetophenone derivatives from 2,3-diacetoxy-α-diaza-acetophenone. J. Org. Chem. **1955**, *20*, 38.
11. (a) Ansell, M.F.; Godsen, A.F.; Leslie, V.J.; Wilson, D.A. Reactions of *o*-benzoquinones with cyclopentadiene. J. Chem. Soc. (C) **1971**, 1401; (b) Ansell, M.F.; Bignold, A. A novel mode of dimerization of benzoquinone. J. Chem. Soc., Chem. Commun. **1971**, 1562.
12. Lee, J.; Li, J.-H.; Oya, S.; Snyder, J.K. Asymmetric synthesis of tanshindiol-A. J. Org. Chem. **1992**, *57*, 5301.
13. Danishefsky, S.; Schuda, F.P.; Carutherus, W. A dramatic solvent effect in the Diels-Alder reactions of *o*-benzoquinones, Diels–Alder reaction using in situ generated quinines. J. Org. Chem. **1977**, *42*, 2179.
14. Kraus, G.A.; Taschner, M.J. Diels–Alder reactions using in situ generated quinines. J. Org. Chem. **1980**, *45*, 1174.
15. Johnson, R.A.; Sharpless, K.B. *Catalytic Asymmetric Synthesis*; Ojima, J., Ed.; VCH: Weinheim, New York, 1993; 103.
16. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley and Sons: New York, 1976; 86.
17. Al-Hamdany, R.; Ali, B. Diels–Alder reaction of *o*-benzoquinone with acyclic dienes. J. Chem. Soc. Chem. Commun. **1978**, 397.
18. Nair, V.; Kumar, S. Diels–Alder reactions of *o*-benzoquinone with acyclic dienes. J. Chem. Soc. Perkin. Trans. I **1996**, 443.
19. Gore, V.K.; Desai, S.R.; Mayalvaganan, T.; Padmakumar, R.; Hadimani, S.B.; Bhat, S.V. Convenient synthesis of decalin systems of bioactive terpenoids. Tetrahedron **1993**, *49* (13), 2767.
20. Maity, G.; Roy, S.L. Ceric ammonium nitrate catalyzed protection of alcohols by 3,4-dihydro-2-H-pyran. Synth. Commun. **1993**, *23*, 1667.

Received in the USA July 12, 2004