Tosylhydrazone 25b. A mixture of 30 mg (0.1 mmol) of ketone **25a**[4] and 18.6 mg (0.1 mmol) of (*p*-tolylsulfonyl)hydrazine in 2 mL of tetrahydrofuran was stirred at room temperature for 24 h. Evaporation of the solvent and chromatography (1:1 hexane–ethyl acetate) of the residue gave 46 mg (98%) of colorless, crystalline hydrazone **25b**: mp 183–184 °C (CH_2Cl_2–C_6H_{14}); UV λ_{max} 207 nm (ϵ 22 510), 220 (27 510), 270 (13 510), 277 (14 100), 281 (14 150), 294 (13 190); IR NH 3295 (w), C=N 1600 (m), SO_2 1375 (s), 1170 (s) cm^{-1}; ^1H NMR δ 2.17 (s, 3, Me), 2.38 (s, 3, aryl Me), 7.25–8.24 (m, 13, aryl Hs), 7.73 (s, 1, H-2); MS *m/e* 467 (M^+, 20%), 312 (58), 284 (40), 283 (44), 171 (88), 170 (26), 143 (61), 142 (base), 139 (31), 115 (77), 92 (30), 91 (62), 77 (54); exact mass 467.1000, calcd for $C_{23}H_{21}N_3O_4S_2$ 467.0972.

X-ray Crystal Structure Analysis of Compound 21. $C_{25}H_{25}NO_5S$, M_r = 451.55, triclinic, a = 10.803 (3) Å, b = 12.445 (3) Å, c = 9.831 (3) Å, α = 109.85 (2)°, β = 109.39 (2)°, γ = 65.34 (2)°, V = 1101.4 Å^3, Z = 2, D_{calcd} = 1.361 g cm^{-3}, μ(Cu Kα radiation, λ = 1.5418 Å), = 15.8 cm^{-1}. Space group $P1(C_1^1)$ or $P\bar{1}(C_{1i}^1)$ from the Laue symmetry, shown to be the latter by structure solution and refinement. Sample dimensions: 0.16 × 0.22 × 0.54 mm.

Preliminary unit-cell parameters and space group information were obtained from oscillation, Weissenberg, and precession photographs. One hemisphere of intensity data (3911 nonequivalent reflections) was recorded on an Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, incident-beam graphite monochromator; ω–2θ scans, θ_{max} = 67°), and those 3489 reflections with $I > 3.0\sigma(I)$ were retained for the structure analysis. The data were corrected for the usual Lorentz and polarization effects, and an empirical absorption correction (T_{max}:T_{min} = 1.00:0.91) was also applied. Refined unit-cell parameters were derived from the diffractometer setting angles for 25 reflections (59° < θ < 67°) widely separated in reciprocal space.

The crystal structure was solved by direct methods,[10] assuming at the outset that $P\bar{1}$ was the correct choice of space group. Approximate non-hydrogen atom coordinates were obtained from an *E* map. Hydrogen atoms were all located in a difference Fourier synthesis evaluated following several rounds of full-matrix least-squares adjustment of non-hydrogen atom positional and anisotropic temperature factor parameters. With the inclusion of hydrogen atom positional and isotropic thermal parameters as variables in the subsequent least-squares iterations, the refinement converged at R = 0.036 (R_w = 0.057).[11] Final atomic positional and thermal parameters are in Tables S-1 to S-3.[12]

Neutral atom scattering factors used in the structure-factor calculations were taken from ref 19. In the least-squares iteractions, $\sum w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized.

Acknowledgment. Support of this work by the World Health Organization, Special Programme of Research, Development and Research Training in Human Reproduction, is acknowledged gratefully. E.W., P.D.R.M., and S.R.P. are indebted to Mr. D. Verdon for technical assistance in several experiments.

Supplementary Material Available: Tables of non-hydrogen atom positional and anisotropic temperature factor parameters, hydrogen atom positional and isotropic thermal parameters, interatomic distances, bond angles, and torsion angles for **21** (10 pages). Ordering information is given on any current masthead page.

(19) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Rearrangement of Homobrendane Derivatives. Total Syntheses of Racemic Copacamphor, Ylangocamphor, and Their Homologues

T. R. Kasturi* and R. Chandra

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, India

Received December 7, 1987

Rearrangement of a homobrendane derivative **8a** to perhydro-1,4-methanoindene system **9a** could be brought about either by *p*-toluenesulfonic acid or boron trifluoride etherate. Similarly, rearrangement of **8b–d** led to the formation of perhydro-1,4-methanoindene derivatives **9b–d**. On the basis of the location of substituents in the starting material and the product, a probable mechanistic pathway has been suggested. The appropriate modification of the peripheral functionalities in **9** led to efficient total syntheses of (±)-copacamphor (**15a**), (±)-ylangocamphor (16a), and their homologues **15b** and **16b**.

In the course of our study pertaining to the total synthesis of B-seco steroids,[1] we observed that seco diones of the type **3** yielded unusual products depending on the acid and solvent employed.[2] While the reaction of *p*-toluenesulfonic acid (*p*-TsOH) afforded the desired pentaenones, MeOH–HCl reaction of the seco diones **3a** and **3c** yielded isomeric bicyclo[3.2.1]octane derivatives **4** and **5** as the major products along with the tricyclic hydroxy ketone **6**. Conclusive structural assignments and correlation with diagnostic NMR patterns for the isomeric compounds **4** and **5** have been published.[3] The tricyclic hydroxy ketone **6**, a homobrendane derivative, was obtained in 20% yield, and its structure was unambiguously established by spectral as well as X-ray crystal structure analyses.[4,5] Similar homobrendane system has been reported to be formed during acid-[6] or base-catalyzed[7] cyclization. The present paper describes a novel rearrangement of such a homobrendane derivative to the perhydro-1,4-methanoindene skeleton culminating in a facile synthesis of the natural product precursor (±)-copacamphor (**15a**), its C_5-epimer, (±)-ylangocamphor (**16a**), and their C_1-homologues **15b** and **16b**.

Rearrangement. An acid-catalyzed rearrangement of the homobrendane system can be initiated only if a carbocation can be generated at a position other than the

(1) (a) Kasturi, T. R.; Ramachandra, R. *Indian J. Chem.* **1975**, *13*, 206. (b) Kasturi, T. R.; Madhava Reddy, S. *Indian J. Chem., Sect. B* **1982**, *21B*, 8.

(2) Kasturi, T. R.; Madhava Reddy, S.; Ramachandra, R.; Abraham, E. M. *Indian J. Chem., Sect. B* **1980**, *19B*, 433.

(3) Kasturi, T. R.; Parvathi. S. M.; Madhava Reddy, S.; Mohan. M. B.; Venkatesan, K. *J. Org. Chem.* **1981**, *46*, 5007.

(4) Kasturi, T. R.; Ramachandra, R.; Damodaran, K. M.; Kalyani Vijayan, *Tetrahedron Lett.* **1972**, 5059.

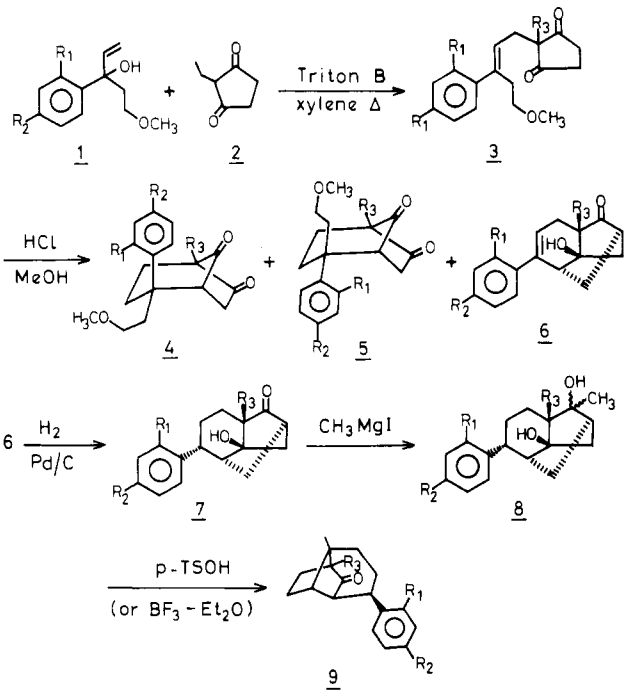
(5) Kasturi, T. R.; Ramachandra, R.; Damodaran, K. M. *Tetrahedron.* **1974**, *30*, 3471. (b) Kasturi, T. R.; Ramachandra, R. *Indian J. Chem.* **1975**, *13*, 9.

(6) Banerjee, D. K.; Kasturi, T. R.; Saibaba, R.; Sarkar, A. *Proc.-Indian Acad. Sci., Chem. Sci.* **1985**, *95*, 439.

(7) Danishefsky, S., Migdalof, B. H. *Tetrahedron Lett.* **1969**, 4331.

0022-3263/88/1953-3178$01.50/0

Scheme I[a]



[a] **a**, $R_1 = R_2 = OCH_3$, $R_3 = CH_3$; **b**, $R_1 = R_2 = OCH_3$, $R_3 = C_2H_5$; **c**, $R_1 = H$, $R_2 = OCH_3$, $R_3 = CH_3$; **d**, $R_1 = H$, $R_2 = OCH_3$, $R_3 = C_2H_5$.

bridgehead. The tertiary alcohol resulting from a Grignard addition to the carbonyl function in **7** could serve as a suitable substrate poised for skeletal rearrangement.

Grignard reaction of the hydroxy ketone **7a** with methylmagnesium iodide gave the diol **8a** quantitatively. The IR [ν_{max} 3460 cm^{-1} (br) and the absence of the carbonyl stretching] and the ^1H NMR [δ 1.25 (s, 3 H)] of the product confirmed its structure. The diol **8a** was refluxed in benzene with catalytic amount of *p*-TsOH for an hour, and the reaction was monitored by TLC, which indicated the formation of a new less-polar product. After the usual workup, a white crystalline solid was obtained in 97% yield as the sole product.[8] IR spectrum indicated the presence of a five-membered ring carbonyl (ν_{max} 1735 cm^{-1}). The presence of two quaternary methyls (singlets at δ 0.92 and 0.99), two methoxyl groups (singlet at δ 3.80) and 1,2,4-trisubstituted benzene ring [δ 6.30–6.54 (m, 2 H) and 7.20 (d, 1 H)] was evident from the ^1H NMR spectrum. The mutual coupling of the two signals at δ 2.56 (d, 1 H) and 3.46 (dd, J = 4 and 8 Hz, 1 H) indicated the presence of the group $CH_2CH(Ar)CHC(=O)$. On the basis of the spectral data, several probable structures could be considered. A single-crystal X-ray diffraction study unambiguously indicated[9] the skeletal structure **9a** for the new compound. However, due to the poor quality of the crystal, the R factor (0.165) could not be improved.

With a view to obtaining a better crystal for X-ray diffraction studies and also to study the mechanism and generality of this novel transformation, three additional substrates **6b–d** which had differently substituted aryl rings and angular alkyl groups were synthesized (Scheme I). The seco diones **3b** and **3d** were prepared from the appropriate vinylcarbinols 1 by the direct condensation of 2-ethylcyclopentane-1,3-dione (**2**) in the presence of catalytic amount of Triton B in refluxing xylene.[10] The product obtained was purified by column chromatography over neutral alumina. The seco diones, obtained as pale yellow viscous oils, were identified by the occurrence of a split carbonyl absorption in IR (ν_{max} 1765 and 1725 cm^{-1}, characteristic of 2,2-disubstituted cyclopentane-1,3-dione moiety[11]) and by ^1H NMR spectra. In the case of the seco dione **3d** the presence of the *E* (major) and *Z* (minor) isomers was evident from their ^1H NMR spectra as reported earlier.[12] Since both the isomers yielded the same ratio of products in the acid-catalyzed cyclization, no attempt was made to separate the two isomers in the present case. However, in the case of the seco dione **3b**, only the *E* isomer was formed.

The gummy residue obtained from the methanolic hydrogen chloride reaction of the seco dione **3b** showed the presence of mainly three major components (TLC), two of them less polar and the third one more polar than the starting material. The individual components were separated by column chromatography over neutral alumina followed by preparative TLC. They were further purified by crystallization from a hexane–benzene mixture. The less polar compounds showed similar spectral characteristics (IR, split carbonyl at 1765 and 1725 cm^{-1}; ^1H NMR no olefinic proton). Mass spectral and elemental analyses confirmed that these two compounds were isomeric with one another and also with the seco dione **3b**. On the basis of the above data and the previous report,[2,3] the isomeric exo and endo bicyclo[3.2.1]octane-6,8-dione structures **4b** and **5b** were assigned to them. The more polar compound showed IR absorptions at 3400 (s) and 1735 cm^{-1} and ^1H NMR signals at δ 1.03 (CH_2CH_3), 1.68–3.00 (m, 10 H), and 5.84 (t, olefinic proton), which were in accordance with those of the reported homobrendane system,[4,5] and hence, structure **6b** was assigned to this compound.

In the case of the seco dione **3d**, only two compounds were obtained in the methanolic hydrogen chloride reaction. On the basis of the splitting pattern in the ^1H NMR spectrum, the less polar compound was characterized as the endo isomer **5d**. No trace of the other isomer was seen. On the basis of the spectral characteristics, the more polar compound obtained in the reaction was assigned structure **6d**.

Catalytic hydrogenation of the tricyclic hydroxy ketones **6b–d** using 10% Pd–C gave the dihydro compounds **7b–d**. Grignard reaction with methylmagnesium iodide afforded the diols **8b–d** quantitatively. *p*-TsOH–benzene refluxing or BF_3·Et_2O reaction of the diols **8b–d** resulted in each case in the formation of a less polar compound whose spectral properties were similar to those of **9a**, and hence, structures **9b**, **9c**, and **9d** were respectively assigned to them. The structure and stereochemistry of the compound **9d** was confirmed by X-ray diffraction study.[9]

Mechanism. A myriad of acid-catalyzed rearrangements of complex polycyclic terpene skeletons are reported in literature.[13] A tentative mechanism for this transformation has been postulated (Scheme II) based on the structural similarity of our substrate and the product with

(8) The same reaction could also be brought about more efficiently by using BF_3·Et_2O at room temperature in 5 minutes.

(9) Kasturi, T. R.; Chandra, R.; Ramachandra, R.; Madhava Reddy, S.; Venkatesan, K., Srikrishnan, T.; Guru Row, T. N.; Purnick, V. G.; Tavale, S. S. *J. Chem. Soc., Chem. Commun.* **1987**, 75.

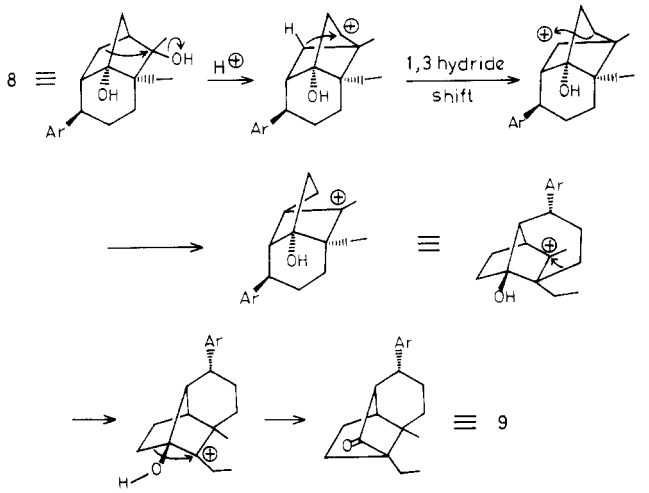
(10) (a) Ananchenko, S. N.; Leonov, V. N.; Platonova, A. V.; Torgov, I. V. *Dokl. Akad. Nauk SSSR* **1960**, *175*, 73. (b) Ananchenko, S. N.; Limanov, V. Ye.; Rzheznikov, V. N.; Torgov, I. V. *Tetrahedron* **1962**, *18*, 1355.

(11) Wheeler, O. H.; Covarrubias, C. B. *Can. J. Chem.* **1962**, *40*, 1224.

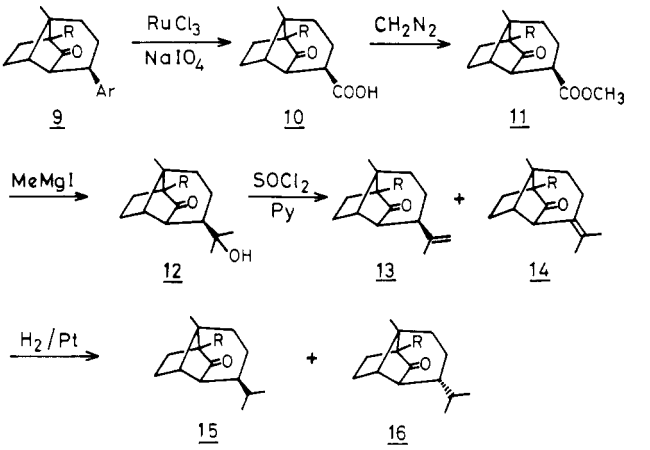
(12) Kasturi, T. R.; Ramachandra, R. *Indian J. Chem.* **1975**, *13*, 429.

(13) (a) *Terpenoids and Steroids*, Specialist Periodical Reports: The Chemical Society: London, 1974; Vol. 4. (b) *Progress in the Chemistry of Organic Natural Products*; Herz, W., Grisebach, H., Kirby, G. W., Eds.; Springer: New York, **1981**; Vol. 40, pp 49–104.

Scheme II



Scheme III[a]



[a] **a**, R = CH_3; **b**, R = C_2H_5.

that of a related rearrangement.[14] The location of the angular ethyl group of the substrate **6d** at the bridgehead position of the product **9d** further corroborates this proposed sequence of bond migrations.[15] The presence and the participation of the second hydroxy function in the molecule precludes any equilibration of the carbocation intermediate resulting in an exclusive formation of the product.

Syntheses of (±)-Copacamphor (15a) and (±)-Ylangocamphor (16a) and Their C_1-Homologues 15b and 16b. The perhydro-1,4-methanoindene skeleton **9** is present in many natural products namely the sesquiterpenes forming the "copa" and "ylango" series[16] such as copacamphor (**15a**) and ylangocamphor (**16a**). The related sesquiterpene alcohol copaborneol[17,18] occurs in *Pinus silverstris L.*[19] and Swedish Sulphate Turpentine.[20] Various syntheses of these sesquiterpenes have been reported.[21,22] In most of these syntheses, appropriate monocyclic or bicyclic precursors were modified via sequential annulation reactions to construct the target molecule. The acid-catalyzed rearrangement of the homobrendane derivative discussed above, by serendipity, provides a direct entry to the carbocyclic structure germane to this class of terpenes. We now describe functional modification of the skeletal precursor **9** to the desired natural product precursors. An important step in this transformation is the oxidation of the aromatic ring to a carboxylic acid (Scheme III). Aromatic rings are known to be cleaved with various oxidizing agents.[23-28] Oxidation[26] of the compound **9a** with *cis*-$(bpy)_2{\cdot}RuCl_2{\cdot}2H_2O$ gave the corresponding acid **10a** along with the unreacted starting material. The yield of the acid could not be improved even after increasing the reaction time. When the oxidation of **9a** was carried out following the Sharpless procedure[28] using $RuCl_3$ and $NaIO_4$ in CCl_4–CH_3CN–H_2O, the acid **10a** was obtained in 90% yield. Diazomethane esterification of the acid **10a** afforded the methyl ester **11a**. The structure of the ester **11a** was evident by its IR (ν_{max} 1735 and 1730 cm^{-1}) and ^1H NMR spectra (singlet at δ 3.64 and absence of aromatic signals). Treatment of the ester **11a** with excess methylmagnesium iodide afforded the alcohol **12a**. IR absorption (ν_{max} 3600 and 1740 cm^{-1}) and ^1H NMR signals [δ 1.13 (s), 1.20 (s), and the absence of the ester methoxyl at δ 3.64] confirmed its structure. The carbonyl function in the molecule survived the reaction probably due to steric hindrance. Dehydration of the alcohol using thionyl chloride–pyridine as reported by Money et al.[22b] provided a mixture of the two olefins **13a** and **14a** in the ratio of 7:3 (estimated by GC and NMR). Hydrogeneration[29] of the mixture of alkenones over $PtO_2/NaBH_4$ in ethyl acetate–acetic acid (19:1) afforded (±)-copacamphor (**15a**) and (±)-ylangocamphor (**16a**) in the ratio of 3:2, which were separated by preparative TLC. The structures of these compounds were confirmed by comparison with authentic IR, NMR, and mass spectra.[30]

Following a similar sequence of reactions, the syntheses of (±)-C_1-homocopacamphor (**15b**) and C_1-homoylangocamphor (**16b**) were achieved starting from **9d**. The mixture of the two compounds obtained in the ratio of 3:2

(14) McMurry, J. E. *J. Org. Chem.* **1971**, *36*, 2826.
(15) For the sake of clarity a discrete mechanism has been shown (Scheme II). It could as well be a concerted mechanism also.
(16) *The Total Synthesis of Natural Products*; ApSimon, J. W., Ed.; Wiley: New York, **1982**; Vol. 5, pp 429–445.
(17) Kolbe, M.; Westfelt, L. *Acta Chem. Scand.* **1967**, *21*, 585.
(18) Kolbe-Haugwitz, M.; Westfelt, L. *Acta Chem. Scand.* **1970**, *24*, 1623.
(19) Westfelt, L. *Acta Chem. Scand.* **1966**, *20*, 2829.
(20) Westfelt, L. *Acta Chem. Scand.* **1966**, *20*, 2841.
(21) (a) Piers, E.; Britton, R. W.; Keziere, R. J.; Smillie, R. D. *Can. J. Chem.* **1971**, *49*, 2620. (b) Piers, E.; Britton, R. W.; Keziere, R. J.; Smillie, R. D. *Can. J. Chem.* **1975**, *53*, 2827.
(22) (a) Hodgson, G. L.; MacSweeney, D. F.; Money, T. *Tetrahedron Lett.* **1972**, 3683. (b) Hodgson, G. L.; MacSweeney, D. F.; Money, T. *J. Chem. Soc, Perkin Trans. 1* **1973**, 2113. (c) Eck, C. R.; Hodgson, G. C.; MacSweeney, D. F.; Mills, R. W.; Money, T. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1938.
(23) Deno, N. C.; Greigger, B. A.; Messner, L. A.; Meyer, M. D.; Stroud, S. G. *Tetrahedron Lett.* **1977**, 1703. (b) Liotta, R.; Hoff, W. S. *J. Org. Chem.* **1980**, *45*, 2887.
(24) Klein, H.; Steinmetz, A. *Tetrahedron Lett.* **1975**, 4249.
(25) Pyatnitskii, Yu. I. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 762.
(26) Chakraborti, A. K.; Banik, B. A.; Ghatak, U. R. *Indian J. Chem., Sect. B* **1984**, *23B*, 291.
(27) Caputo, J. A.; Fuchs, R. *Tetrahedron Lett.* **1967**, 4729. (b) Platak, D. M.; Herbst, G.; Wicha, S.; Caspi, E. *J. Org. Chem.* **1969**, 34, 116. (c) Wolfe, S.; Hasan, S. K.; Campbell, J. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1420. (d) Ayres, D. C.; Hassain, A. M. M. *J. Chem. Soc., Chem. Commun.* **1972**, 428. (e) Spitzer, U. A.; Lee, G. D. *J. Org. Chem.* **1974**, *39*, 2468. (f) Lee, G. D. In *Oxidation in Organic Chemistry*; Trahanovsky, S. W., Ed., Academic: New York, **1973**; pp 194–196; Part B.
(28) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, B. K. *J. Org. Chem.* **1981**, *46*, 3936.
(29) For the use of sodium borohydride to reduce platinum salts and other metals forming reactive hydrogenation catalyst, see: (a) Brown, H. C.; Brown, C. A. *Tetrahedron* **1966**, 146. (b) Brown, C. A.; Brown, H. C. *J. Org. Chem.* **1966**, *31*, 3989. (c) Brown, C. A. *J. Am. Chem. Soc.* **1969**, *91*, 5901; *J. Chem. Soc., Chem. Commun.* **1970**, 139.
(30) We thank Professor Thomas Money, Department of Chemistry, University of British Columbia, for providing authentic spectra of the two compounds (±)-copacamphor and (±)-ylangocamphor. Heartfelt thanks are due to Dr. A. Sarkar, Dr. R. Saibaba, and Dr. S. K. Jayaram for useful discussions. One of the authors (R.C.) thanks CSIR (New Delhi) for financial assistance.

was separated by preparative TLC and characterized by spectral data.

Thus, a short and efficient syntheses of the natural product precursor **15a**, its C_5-epimer, and their homologues have been successfully achieved.

Experimental Section

All melting points and boiling points reported herein are uncorrected. The IR spectra were taken on Perkin–Elmer Model 781 spectrophotometer. The NMR spectra were recorded on a Varian T-60, a Varian HA-100, a Jeol FX-90Q, or a Bruker WH-270 MHz NMR spectrometer. Chemical shifts are quoted relative to TMS ($\delta = 0$) as internal standard. The mass spectra were recorded on Jeol MS-DX 303 spectrometer operating at 70 eV fitted with a built-in inlet system. GLC analysis was performed on a Chemito 3800 gas chromatograph using 10% Carbowax QF_1 column of size 6 ft × $^1/_8$ in. All organic extracts were dried over Na_2SO_4. Analytical and preparative-layer chromatography were carried out using silica gel supplied by BDH (Bombay) or Acme synthetic chemicals (Bombay). For column chromatography, Acme silica gel and BDH neutral alumina were used.

General Procedure for the Preparation of Seco Diones 3. A mixture of vinyl chloride **1** (0.05 mol), 2-ethylcyclopentane-1,3-dione (**2**) (0.06 mol), Triton B (3.5 mL), and xylene (80 mL) was refluxed with azeotropic removal of water for 12–16 h. The cooled reaction mixture was diluted with benzene, washed successively with water, cold aqueous KOH, and water, and dried. The gummy residue obtained after the removal of solvent was purified by column chromatography over neutral (1:20) alumina (benzene–$CHCl_3$, 1:1) followed by short-path distillation.

2-Ethyl-2-[5-methoxy-3-(2,4-dimethoxyphenyl)pent-2-enyl]cyclopentane-1,3-dione (3b). The vinylcarbinol **1a** (12.6 g) on condensation with the dione **2** (7.56 g) in the presence of Triton B (3.5 mL) yielded the seco dione **3b** (13.6 g, 76%): 200–210 °C (2 mm) (bath temperature); IR (neat) ν_{max} 1765 and 1725 cm^{-1} (split carbonyl band); ^1H NMR ($CDCl_3$) δ 0.77 (t, J = 8.6 Hz, 3 H), 1.73 (q, J = 8.6 Hz, 2 H), 2.48–2.66 (t, J = 8.6 Hz, on which a doublet J = 8.6 Hz is superimposed, 4 H), 2.66 (s, 4 H), 3.17 (t, J = 8.6 Hz, 2 H), 3.22 (s, 3 H), 3.74 (s, 3 H), 3.78 (s, 3 H), 5.18 (t, J = 8.6 Hz, 1 H), 6.33–6.45 (m, 2 H), and 6.87 (d, J = 9 Hz, 1 H). Anal. Calcd for $C_{21}H_{28}O_5$: C, 69.97; H, 7.83. Found: C, 69.93; H, 7.81.

2-Ethyl-2-[5-methoxy-3-(*p*-methoxyphenyl)pent-2-enyl]-cyclopentane-1,3-dione (3d). Condensation of the vinylcarbinol **1c** (11.1 g) with the dione **2** (7.56 g) in the presence of Triton B (3.5 mL) yielded the seco dione **3d** (12.1 g, 73%): 192–194 °C (2 mm) (bath temperature); IR (neat) ν_{max} 1765 and 1720 cm^{-1} (split carbonyl band); ^1H NMR ($CDCl_3$) δ 0.67, 0.79 (t, J = 8.6 Hz, 3 H), 1.66, 1.75 (q, J = 8.6 Hz, 2 H), 2.51–2.80 (m, 4 H), 2.65 (s, 4 H), 3.25 (t, J = 8.6 Hz, 2 H), 3.25, 3.26 (s, 3 H), 3.79, 3.82 (s, 3 H), 5.30, 5.39 (t, J = 8.6 Hz, 1 H), and 6.76–7.27 (2 AB q, 4 H). Anal. Calcd for $C_{20}H_{26}O_4$: C, 73.70; H, 7.93. Found: C, 73.65; H, 7.93.

General Procedure for the Methanolic Hydrogen Chloride Reaction of the Seco Diones 3. To a solution of the seco dione **3** (0.01 mol) in dry MeOH (45 mL) was added dry MeOH (40 mL) saturated with dry HCl gas. The solution was left at room temperature for 4 h. MeOH was removed in vacuo, and the residue was extracted with ether. The ether extract was successively washed with water, aqueous $NaHCO_3$, and water and dried. The residue, obtained from removal of the solvent, was subjected to column chromatography over neutral alumina (1:20) followed by preparative TLC. The compounds were further purified by crystallization.

MeOH–HCl Reaction of 3b. The seco dione **3b** (10 g) on methanolic HCl reaction afforded three products.

Fraction 1 (hexane–benzene, 2:1) yielded the least polar compound, 5-ethyl-2-*exo*-(2-methoxyethyl)-2-*endo*-(2,4-dimethoxyphenyl)bicyclo[3.2.1]octane-6,8-dione (**5b**, 3.75 g, 38%): mp 107 °C (benzene–hexane); IR (Nujol) ν_{max} 1760 and 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (t, J = 8.6 Hz, 3 H), 1.53–2.06 (m, 7 H), 2.32 (d, J = 4.3 Hz, 2 H), 2.40–3.00 (m, 3 H), 3.08 (s, 3 H), 3.74 (t, J = 4.3 Hz, 1 H), 3.81 (s, 6 H), 6.40–6.47 (m, 2 H), and 7.04 (d, J = 10 Hz, 1 H). Anal. Calcd for $C_{21}H_{28}O_5$: C, 69.97; H, 7.83. Found: C, 69.89; H, 7.83.

Fraction 2 (hexane–benzene, 1:1) gave 5-ethyl-2-*endo*-(2-methoxyethyl)-2-*exo*-(2,4-dimethoxyphenyl)bicyclo[3.2.1]octane-6,8-dione (**4b**, 600 mg, 6%): mp 133 °C (benzene–hexane); IR (Nujol) ν_{max} 1760 and 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72 (t, J = 8.6 Hz, 3 H), 1.40–1.96 (m, 6 H), 2.20–2.70 (m, 3 H), 2.83–3.06 (m, 3 H), 3.12 (s, 3 H), 3.80 (s, 3 H), 3.85 (s, 3 H), 3.96 (d, J = 8.6 Hz, 1 H), 6.35–6.54 (m, 2 H) and 7.00 (d, J = 9 Hz, 1 H). Anal. Calcd for $C_{21}H_{28}O_5$: C, 69.97; H, 7.83. Found: C, 69.96; H, 7.83.

Fraction 3 (5% ethyl acetate–$CHCl_3$) gave the tricyclic hydroxy ketone, 7a-ethyl-3a-hydroxy-5-(2,4-dimethoxyphenyl)-2β,3,3aβ,4β,7,7aβ-hexahydro-2,4-methano-1*H*-inden-1-one (**6b**, 2.5 g, 27%): mp 122 °C (benzene–hexane); IR (Nujol) ν_{max} 3400 (s), 1735, 1610, and 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, J = 6 Hz, 3 H), 1.12–1.19 (m, 1 H), 1.68–3.00 (m, 10 H), 3.78 (s, 3 H), 3.79 (s, 3 H), 5.57 (t, J = 4.5 Hz, 1 H), 6.40–6.48 (m, 2 H) and 6.85 (d, J = 9 Hz, 1 H). Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 73.13; H, 7.31.

MeOH–HCl Reaction of 3d. The seco dione **3d** (10 g) was treated with MeOH–HCl to give a mixture of two compounds. The less polar compound (hexane–benzene, 1:1) was shown to be 5-ethyl-2-*exo*-(2-methoxyethyl)-2-*endo*-(*p*-methoxyphenyl)bicyclo[3.2.1]octane-6,8-dione (**5d**, 4.25 g, 43%): 200–203 °C (1 mm) (bath temperature); IR (neat) ν_{max} 1760 and 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, J = 8.6 Hz, 3 H), 1.54–2.13 (m, 8 H), 2.38 (d, J = 4 Hz, 2 H), 2.91–3.32 (m, 3 H), 3.13 (s, 3 H), 3.81 (s, 3 H) and 6.82–7.19 (AB q, J = 12 Hz, 4 H). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.7; H, 7.93. Found: C, 72.7; H, 7.93.

The more polar compound (5% ethyl acetate–$CHCl_3$) was the hydroxy ketone, 7a-ethyl-3a-hydroxy-5-(*p*-methoxyphenyl)-2β,3,3aβ,4β,7,7aβ-hexahydro-2,4-methano-1*H*-inden-1-one (**6d**, 2.5 g, 28%): mp 139 °C (benzene–hexane); IR (Nujol) ν_{max} 3380 (s), 1735, 1610, and 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (t, J = 7 Hz, 3 H), 1.18–1.30 (m, 1 H), 3.76 (s, 3 H), 5.84 (t, J = 4 Hz, 1 H), and 6.72–7.24 (AB q, J = 9 Hz, 4 H). Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.45; H, 7.41.

5-Ethyl-3a-hydroxy-5-(2,4-dimethoxyphenyl)-(2β,3aβ,4β,5β,7aβ)-octahydro-2,4-methano-1*H*-inden-1-one (7b). Hydrogenation of the tricyclic hydroxy ketone **6b** (2 g) in MeOH (50 mL) was carried out by using 10% Pd–C (500 mg) catalyst till no more hydrogen was absorbed. The catalyst was filtered off and washed with MeOH, and the solvent was removed to give the saturated hydroxy ketone **7b** (1.95 g, 97%), which was crystallized from a benzene–hexane mixture: mp 143 °C; IR (Nujol) ν_{max} 3400 and 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, J = 6 Hz, 3 H), 1.20–2.65 (m, 13 H), 3.20–3.50 (br s, 1 H, OH), 3.75 (s, 3 H), 3.78 (s, 3 H), 6.23–6.45 (m, 2 H) and 6.78–7.00 (d, J = 9 Hz, 1 H). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.65; H, 7.91.

7a-Ethyl-3a-hydroxy-5-(*p*-methoxyphenyl)-(2β,3aβ,4β,-5β,7aβ)-octahydro-2,4-methano-1*H*-inden-1-one (7d). Hydrogenation of the hydroxy ketone **6d** (2g) was carried out as mentioned above by using MeOH (50 mL) and 10% Pd–C (500 mg) to afford the dihydro compound **7d** (1.98 g, 98%): mp 157 °C (benzene–hexane); IR (Nujol) ν_{max} 3380 and 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (t, J = 4 Hz, 3 H), 1.20–2.60 (m, 13 H), 2.68–3.18 (br s, 1 H), 3.71 (s, 3 H), and 6.62–7.16 (AB q, J = 9 Hz, 4 H). Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97: H, 8.05. Found: C, 75.92; H, 8.03.

General Procedure for the Grignard Reaction of 7 with Methylmagnesium Iodide. A solution of the dihydro ketone **7** in a mixture of absolute THF and ether was added during 30 min to a solution of methylmagnesium iodide (3 equiv) in dry ether at 0 °C under nitrogen atmosphere, and the mixture was stirred at room temperature for 2 h and refluxed for 30 min. The reaction mixture was cooled (0 °C) and decomposed by gradual addition of ice-cold NH_4Cl solution. The layers were separated, the aqueous layer was extracted twice with ether, and the combined ether extract was washed with water and brine and dried. Removal of the solvent yielded the tricyclic diol **8**, which was further purified by preparative TLC.

5-(2,4-Dimethoxyphenyl)-1,7a-dimethyl-(2β,3aβ,4β,5β,-7aβ)-octahydro-2,4-methano-1*H*-indene-1,3a-diol (8a). The dihydro hydroxy ketone **7a** (1.95 g) was treated with methylmagnesium idodide to afford the diol **8a** as an oil (1.95 g, 96%): IR (neat) ν_{max} 3460 (br), 1610, and 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (s, 3 H), 1.25 (s, 3 H), 1.40–2.60 (m, 11 H), 3.10–3.55 (2 br

s, 2 H, OH), 3.79 (s, 6 H), 6.30–6.50 (m, 2 H), and 7.10 (d, J = 7 Hz, 1 H). Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.46. Found: C, 72.25; H, 8.46.

7a-Ethyl-5-(2,4-dimethoxyphenyl)-1-methyl-(2β,3aβ,4β,5β,7aβ)-octahydro-2,4-methano-1*H*-indene-1,3a-diol (8b). Grignard reaction of the dihydro hydroxy ketone **7b** (1.93 g) with methylmagnesium iodide gave the diol **8b** as an oil (1.93 g, 95%): IR (neat) ν_{max} 3460 (br), 1610 and 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, J = 6 Hz, 3 H), 1.42 (s, 3 H), 1.20–2.42 (m, 13 H), 3.00–3.40 (2 br s, 2 H, OH), 3.78 (s, 6 H), 6.34–6.54 (m, 2 H), and 7.03–7.23 (d, J = 6 Hz, 1 H). Anal. Calcd for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.78; H, 8.70.

5-(*p*-Methoxyphenyl)-1,7a-dimethyl-(2β,3aβ,4β,5β,7aβ)-octahydro-2,4-methano-1*H*-indene-1,3a-diol (8c). The dihydro ketone **7c** (2 g) was treated with methylmagnesium iodide to afford the diol **8c** as a viscous oil (2g, 95%): IR (neat) ν_{max} 3540 (s), 3440 (s), 1610, and 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3 H), 1.24 (s, 3 H), 1.20–2.23 (m, 11 H), 2.62–3.00 (2 br s, 2 H, OH), 3.72 (s, 3 H), and 6.64–7.20 (AB q, J = 9 Hz, 4 H). Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.45; H, 8.67.

7a-Ethyl-5-(*p*-methoxyphenyl)-1-methyl-(2β,3aβ,4β,5β,7aβ)-octahydro-2,4-methano-1*H*-indene-1,3a-diol (8d). Grignard reaction of the dihydro compound **7d** (1.93 g) with methylmagnesium iodide gave 1.93 g (95%) of **8d** as a viscous oil: IR (neat) ν_{max} 3540 (s), 3500 (s), 1610, and 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 5 Hz, 3 H), 1.37 (s, 3 H), 1.20–2.23 (m, 13 H), 2.62–3.00 (2 br s, 2 H, OH), 3.70 (s, 3 H), and 6.64–7.19 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.89; H, 8.93.

General Procedure for the Rearrangement of the Diols 8. (a) With *p*-TsOH–Benzene. A benzene (30 mL) solution of the diol 8 (1 g) in the presence of catalytic amount of *p*-TsOH (100 mg) was refluxed in an oil bath with stirring for 1 h. The reaction mixture was cooled to room temperature, washed with water, aqueous $NaHCO_3$, and water, and dried. The crude product **9** obtained after the removal of the solvent, was purified by column chromatography over neutral alumina (1:10, $CHCl_3$) followed by crystallization.

(b) With BF_3–Et_2O. A solution of the diol 8 (1 g) in CH_2Cl_2 (25 mL) containing catalytic amount of BF_3–Et_2O (0.5 mL) was stirred at room temperature for 5 min. The reaction mixture was diluted with water, washed with aqueous $NaHCO_3$ and water, and dried. The crude product, obtained after the removal of the solvent, was purified as mentioned above.

5-(2,4-Dimethoxyphenyl)-1,7a-dimethyl-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (9a). Treatment of the diol **8a** (1 g) with *p*-TsOH in benzene or BF_3·Et_2O in CH_2Cl_2 afforded the compound **9a** (0.93 g, 97%): mp 127 °C (benzene–hexane); IR (Nujol) ν_{max} 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.92 (s, 3 H), 0.99 (s, 3 H), 1.04–2.20 (m, 9 H), 2.56 (d, J = 4 Hz, 1 H), 3.46 (dd, J = 4 and 8 Hz, 1 H), 3.80 (s, 6 H), 6.30–6.54 (m, 2 H) and 7.20 (d, J = 9 Hz, 1 H); ^{13}C NMR [($CDCl_3$) off-resonance decoupled] singlets at δ 48.76, 57.21, 124.71, 158.19, 159.22, 222.46; doublets at 35.16, 42.80, 55.58, 98.44, 103.47, 127.85, triplets at δ 23.24, 24.81, 30.34, 31.64, quartets at δ 9.10, 18.80, 55.26 (x2); MS, m/e (relative intensity) 314 (M^+, 30), 177 (100), 151 (50). Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.37; H, 8.38.

1-Ethyl-5-(2,4-dimethoxyphenyl)-7a-methyl-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (9b). The diol **8b** (1 g) on treatment with *p*-TsOH in benzene or BF_3·Et_2O in CH_2Cl_2 afforded the rearranged ketone **9b** (0.93 g, 97%): mp 102 °C (benzene–hexane); IR (Nujol) ν_{max} 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 3 H), 1.06 (t, J = 7.5 Hz, 3 H), 2.51 (d, J = 4 Hz, 1 H), 3.51 (m, 1 H), 3.8 (s, 6 H), 6.44–6.52 (m, 2 H), and 7.18–7.21 (d, J = 9 Hz, 1 H); ^{13}C NMR [($CDCl_3$) off-resonance decoupled] singlets at δ 49.20, 59.67, 124.77, 158.12, 159.29, 221.85; doublets at 35.29, 43.42, 55.71, 98.49, 103.50, 128.79, triplets at δ 19.42, 23.26, 24.49, 28.66, 31.06, quartets at δ 9.60, 18.64, 54.93 (x2); MS, m/e (relative intensity) 328 (M^+, 75), 177 (100), 151 (51). Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.34. Found: C, 76.80; H, 8.30.

5-(*p*-Methoxyphenyl)-1,7a-dimethyl-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (9c). Treatment of the diol **8c** (1 g) with *p*-TsOH in benzene or BF_3·Et_2O in CH_2Cl_2 afforded the rearranged ketone **9c** (0.92 g, 96%): mp 77 °C (benzene–hexane); IR (Nujol) ν_{max} 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3 H), 1.00 (s, 3 H), 1.13–1.94 (m, 9 H), 2.39 (d, J = 4 Hz, 1 H), 3.23 (m, 1 H), 3.79 (s, 3 H), and 6.85–7.29 (AB q, J = 9 Hz, 4 H); ^{13}C NMR [($CDCl_3$) off-resonance decoupled] singlets at δ 43.36, 54.99, 135.11, 157.61, 221.59, doublets at δ 38.78, 42.25, 58.11, 113.65 (x2), 127.35 (x2), triplets at δ 22.87, 24.56, 29.50, 31.32, quartets at δ 9.50, 18.57, 57.20; MS, m/e 284 (M^+), 147, 121. Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.26; H, 8.50.

1-Ethyl-5-(*p*-methoxyphenyl)-7a-methyl-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (9d). The diol **8d** (1 g) was treated with *p*-TsOH in benzene or BF_3·Et_2O in CH_2Cl_2 to give the ketone **9d** (0.91 g, 95%): mp 81 °C (benzene–hexane); IR (Nujol) ν_{max} 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 1.08 (t, J = 7 Hz, 3 H), 2.35 (d, J = 4 Hz, 1 H), 3.27 (m, 1 H), 3.80 (s, 3 H), and 6.85–7.25 (AB q, J = 8 Hz, 4 H); ^{13}C NMR [($CDCl_3$) off-resonance decoupled] singlets at δ 49.39, 60.29, 135.85, 158.01, 222.81, doublets at δ 40.21, 43.20, 58.65, 113.99, 128.28, triplets at δ 19.50, 23.13, 24.65, 28,89, 30.57, quartets at δ 9.61, 18.69, 55.83; MS, m/e (relative intensity) 298 (M^+, 100), 147 (27), and 121 (45). Anal. Calcd for $C_{20}H_{26}O_2$: C, 81.04; H, 8.16. Found: C, 81.15; H, 8.10.

General Procedure for Aromatic Ring Oxidation. A mixture containing the compound **9** (1 mmol), $NaIO_4$ (14.4 equiv), carbon tetrachloride (2 mL), acetonitrile (2 mL), and water (3 mL) was stirred vigorously. To this biphasic solution was added 5 mg (2.2%) of $RuCl_3$·$3H_2O$, and the mixture was stirred vigorously for 4 h at room temperature. After the addition of CH_2Cl_2 (10 mL), the two phases were separated. The aqueous phase was extracted three times with CH_2Cl_2, and the combined CH_2Cl_2 extract was dried. The residue obtained after the concentration was diluted with ether (10 mL), filtered through a Celite pad, and concentrated. The crude product was filtered through a neutral alumina column (1:10, $CHCl_3$), and the product was crystallized. The resulting acid was esterified with diazomethane in ether to afford the methyl ester, which was purified by column chromatography over silica gel (1:10, $CHCl_3$).

1,7a-Dimethyl-8-oxo-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-indene-5-carboxylic Acid (10a). Oxidation of the ketone **9a** (314 mg) with $NaIO_4$ (3.1 g) and $RuCl_3$·$3H_2O$ (5 mg) gave the carboxylic acid **10a** (200 mg, 90%): mp 144 °C (benzene–hexane); IR (Nujol) ν_{max} 3000 (br), 1735, and 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3 H), 0.96 (s, 3 H), 1.25–2.01 (m, 9 H), 2.56 (d, J = 4.5 Hz, 1 H), 2.68 (m, 1 H), and 10.95 (br s, 1 H); ^{13}C NMR [($CDCl_3$) off-resonance decoupled] singlets at δ 48.42, 57.33, 179.46, 221.20, doublets at δ 41.01, 44.46, 53.11, triplets at δ 20.39, 24.56, 28.92, 31.32, quartets at δ 8.95, 18.38; MS, m/e (relative intensity) 222 (M^+), 204, 176, 161, 148, 133, 119, 92 (100), 77, and 69. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.18; H, 8.18.

Diazomethane esterification of the acid afforded the methyl ester **11a** (195 mg, 92%): ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 6 H), 1.15–1.95 (m, 9 H), 2.36 (d, J = 4 Hz, 1 H), 2.74 (m, 1 H), and 3.64 (s, 3 H). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.18; H, 8.53.

1-Ethyl-7a-methyl-8-oxo-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-indene-5-carboxylic Acid (10b). Oxidation of the ketone **9d** (298 mg) with $NaIO_4$ (3.1 g) and $RuCl_3$·$3H_2O$ (5 mg) yielded the acid **10b** (219 mg, 91%): mp 111 °C (benzene–hexane); IR (Nujol) ν_{max} 3000 (br), 1735, and 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 3 H), 1.03 (t, J = 7.2 Hz, 3 H), 1.24–1.95 (m, 11 H), 2.53 (d, J = 3.6 Hz, 1 H), 2.90 (m, 1 H), and 9.33 (br s, 1 H); ^{13}C NMR [($CDCl_3$) off-resonance decoupled] singlets at δ 49.03, 59.76, 179.61, 221.20, doublets at δ 41.10, 45.13, 53.19, triplets at δ 19.12, 20.42, 24.32, 28.74, 29.65, quartets at δ 9.49, 18.47. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.15; H, 8.61.

The corresponding ester **11b** (210 mg, 91%), showed ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3 H), 1.03 (t, J = 7.2 Hz, 3 H), 1.29–1.95 (m, 11 H), 2.45 (d, J = 5.4 Hz, 1 H), 2.81 (m, 1 H), and 3.71 (s, 3 H). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.91; H, 8.86. Found: C, 71.86; H, 8.87.

5-(1-Hydroxy-1-methylethyl)-1,7a-dimethyl-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (12a). Following the general procedure mentioned for the preparation of the diol **8**, Grignard reaction of the ester **11a** (236 mg) was carried out with methylmagnesium iodide (3 equiv) to

afford the hydroxy ketone **12a** (230 mg, 97%): IR (CCl_4) ν_{max} 3620 (s), 3440 (br), and 1740 cm^{-1}; ^1H NMR (CCl_4) δ 0.88 (s, 3 H), 0.93 (s, 3 H), 1.13 (s, 3 H), 1.20 (s, 3 H), 1.24–2.00 (m, 9 H), 2.20 (br s, 1 H), 2.30 (br d, 1 H) and 2.75 (br s, 1 H); MS, *m/e* (relative intensity) 236 (M^+), 95, 93, and 59 (100). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.20; H, 10.24.

1-Ethyl-5-(1-hydroxy-1-methylethyl)-7a-methyl-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (12b). Similarly, the ester **11b** (250 mg) was treated with methylmagnesium iodide (3 equiv) to give the hydroxy ketone **12b** (240 mg, 96%): IR (neat) ν_{max} 3420 and 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (s, 3 H), 1.02 (t, J = 7.2 Hz, 3 H), 1.11 (br s, 3 H), 1.23 (s, 3 H), 1.32–2.00 (m, 12 H), 2.19 (br s, 1 H) and 2.25 (m, 1 H). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.72; H, 10.52.

(±)-1,7a-Dimethyl-5-(1-methylethyl)-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (13a) and (±)-1,7a-Dimethyl-5-(1-methylethylidene)-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (14a). The tricyclic alcohol **12a** (236 mg, 1 mmol) in dry pyridine (2 mL) was treated with thionyl chloride (0.5 mL, 0.049 mmol) at 0 °C for 30 min. The mixture was diluted with hexane. The organic layer was washed with water, aqueous $NaHCO_3$, dilute HCl, and water and dried. Removal of the solvent afforded a mixture of the olefins **13a** and **14a** (200 mg, 92%) in the ratio of 7:3 (GLC and ^1H NMR), purified by passing through a silica gel column: IR (neat) ν_{max} 1740, 1650, and 870 cm^{-1}; ^1H NMR (CCl_4) δ 4.85 (m, 2 H) and 2.94 (s, 1 H).

(±)-1-Ethyl-7a-methyl-5-(1-methylethenyl)-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (13b) and (±)-1-Ethyl-7a-methyl-5-(1-methylethylidene)-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one (14b). Similar dehydration of the tricyclic alcohol **12b** (250 mg, 1 mmol) with thionyl chloride (0.5 mL, 0.049 mmol) and dry pyridine (2 mL) afforded the mixture of olefins **13b** and **14b** (228 mg, 91%) in the ratio 7:3 (GLC, ^1H NMR): IR (neat) ν_{max} 1740, 1650, and 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.87 (m, 2 H) and 2.98 (s, 1 H).

(±)-Copacamphor (15a) [1,7a-Dimethyl-5-(1-methylethyl)-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one] and (±)-Ylangocamphor (16a) [1,7a-Dimethyl-5-(1-methylethyl)-(1α,3aβ,4α,5β,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one. Hydrogenation of the mixture of alkenones **13a** and **14a** (200 mg) over PtO_2 (50 mg) in ethyl acetate, acetic acid (19:1, 20 mL) with sodium borohydride (2.5 g) afforded (±)-copacamphor (**15a**) and (±)-ylangocamphor (**16a**) in a ratio of 3:2. The two compounds were separated by preparative TLC using 5% ethyl acetate–hexane mixture.

(±)-Copacamphor (15a) (118 mg, 60%): IR (neat) ν_{max} 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (d, J = 6.5 Hz, 3 H), 0.90 (s, 3 H), 0.91 (d, J = 6.5 Hz, 3 H), 0.94 (s, 3 H) and 2.16 (m, 1 H); ^{13}C NMR [($CDCl_3$) off-resonance decoupled] singlets at δ 48.16, 57.14, 223.87, doublets at δ 20.92, 31.45, 42.57, 55.32, triplets at δ 24.02, 27.09, 28.72, 43.55, quartets at δ 8.89, 18.51, 20.33, 21.63; MS, *m/e* (relative intensity) 220 (M^+), 149, 135, 124 (100), and 95. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.80; H, 10.92.

(±)-Ylangocamphor (16a) (80 mg, 40%): IR (neat) ν_{max} 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (d, J = 6.5 Hz, 3 H), 0.89 (s, 3 H), 0.90 (s, 3 H), 0.97 (d, J = 6.5 Hz, 3 H), and 2.23 (s, 1 H); ^{13}C NMR [($CDCl_3$) off-resonance decoupled] singlets at δ 48.29, 57.87, 221.92, doublets at δ 29.50, 46.86, 49.66, 54.54, triplets at δ 25.08 (x2), 31.04, 32.10, quartets at δ 8.24, 18.25, 20.13, 21.25; MS, *m/e* 220 (M^+), 124, 110, 95, 93. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.72; H, 10.96.

(±)-C_1-Homocopacamphor (15b) [1-Ethyl-7a-methyl-5-(1-methylethyl)-(1α,3aβ,4α,5α,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one] and (±)-C_1-Homoylangocamphor (16b) [1-Ethyl-7a-methyl-5-(1-methylethyl)-(1α,3aβ,4α,5β,7aβ)-octahydro-1,4-methano-1*H*-inden-8-one]. Hydrogenation of the mixture of alkenones **13b** and **14b** (200 mg) was similarly carried out to give a mixture of (±)-homocopacamphor (**15b**) and (±)-homoylangocamphor (**16b**) in the ratio 3:2, which was separated by preparative TLC using 5% ethyl acetate–hexane mixture.

(±)-C_1-Homocopacamphor (15b) (120 mg, 60%): IR (neat) ν_{max} 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (d, J = 7.5 Hz, 3 H), 0.93 (d, J = 7.5 Hz, 3 H), 0.93 (s, 3 H), 1.03 (t, J = 7.2 Hz, 3 H), and 1.20–2.20 (m, 14 H); MS, *m/e* 234 (M^+). Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.83; H, 11.12.

(±)-C_1-Homoylangocamphor (16b) (80 mg, 40%): IR (neat) ν_{max} 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (d, J = 7.2 Hz, 3 H), 0.93 (s, 3 H), 1.00 (t, J = 7.2 Hz, 3 H), 1.13 (d, J = 7.2 Hz, 3 H), 1.20–2.00 (m, 13 H), and 2.19 (s, 1 H); MS, *m/e* 234 (M^+). Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.91; H, 11.15.

Registry No. (±)-**1a**, 114506-67-1; (±)-**1c**, 114506-68-2; **2**, 823-36-9; **3b**, 114506-69-3; **3d**, 114506-70-6; (±)-**4b**, 114506-71-7; (±)-**5b**, 114506-72-8; (±)-**5d**, 114506-74-0; (±)-**6b**, 114506-73-9; (±)-**6d**, 114506-75-1; (±)-**7a**, 111059-02-0; (±)-**7b**, 114506-76-2; (±)-**7c**, 114579-40-7; (±)-**7d**, 111015-10-2; (±)-**8a** (isomer 1), 114579-41-8; (±)-**8a** (isomer 2), 114579-48-5; (±)-**8b** (isomer 1), 114506-77-3; (±)-**8b** (isomer 2), 114579-49-6; (±)-**8c** (isomer 1), 114506-78-4; (±)-**8c** (isomer 2), 114579-46-3; (±)-**8d** (isomer 1), 114579-42-9; (±)-**8d** (isomer 2), 114579-47-4; (±)-**9a**, 114579-43-0; (±)-**9b**, 114506-79-5; (±)-**9c**, 114506-80-8; (±)-**9d**, 114579-44-1; (±)-**10a**, 114506-81-9; (±)-1/b, 114506-82-0; (±)-**11a**, 114506-83-1; (±)-**11b**, 114506-84-2; (±)-**12a**, 37876-43-0; (±)-**12b**, 114506-85-3; (±)-**13a**, 37876-45-2; (±)-**13b**, 114506-86-4; (±)-**14a**, 37876-46-3; (±)-**14b**, 114506-87-5; (±)-**15a**, 37876-47-4; (±)-**15b**, 114506-88-6; (±)-**16a**, 37876-48-5; (±)-**16b**, 114579-45-2.