(12*S*)-7,12-Secoishwaran-12-ol, a New Type of Sesquiterpene from *Aristolochia indica* Linn[1]

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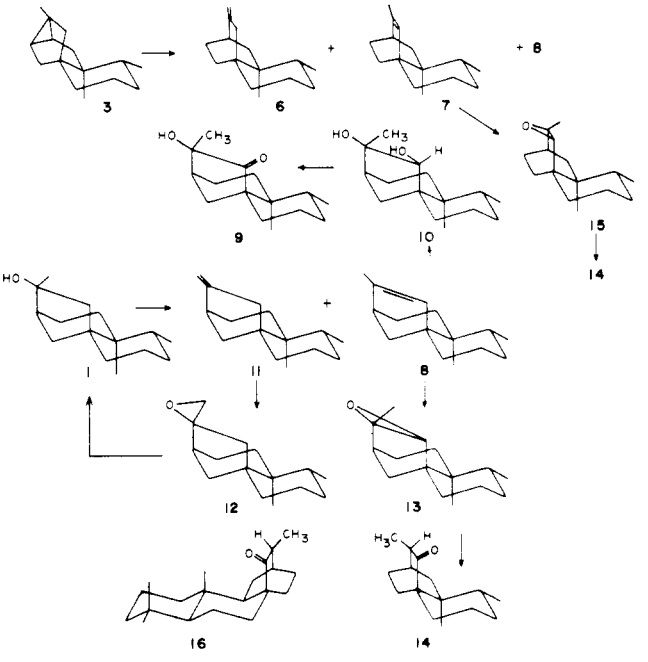
In a program of search for antifertility compounds from Indian medicinal plants, the petroleum ether extract of the roots of *Aristolochia indica* Linn. (Aristolochiaceae) was shown[2] in these laboratories to have 100% interceptive activity in mice at a single dose of 100 mg/kg. The follow-up studies led to the isolation,[3] inter alia, of two isomeric sesquiterpene alcohols. One of them, an active principle,[4] has now been proved to be (12*S*)-7,12-secoishwaran-12-ol (**1**), which represents a new type of sesquiterpene. The other one, mp 103–104 °C, has also been characterized and confirmed by direct comparison as (+)-ledol (**2**), the first aromadendrane derivative encountered in this species.

^{1}H NMR spectrometry revealed that the new sesquiterpene, $C_{15}H_{26}O$, mp 150 °C, is a tertiary alcohol containing three methyl groups present as a CH_3–C–OH [δ 1.28 (3 H, s)], a CH_3–C– [δ 0.87 (3 H, s)] and a CH_3–CH– [δ 0.73 (3 H, d, J = 6 Hz)]. It formed a crystalline monoacetate, while dehydration yielded two isomeric olefins (M^+ at m/e 204) separated by column chromatography. The less polar minor product contained an exocyclic methylene (ν_{max} ($CHCl_3$) 880 cm^{-1}) while the major one was the endo isomer with a —C—CH=C(CH_3)— moiety [δ 5.63 (1 H, br s) and δ 1.70 (3 H, d, J = 1.8 Hz)]. Support for the presence of this grouping was adduced by its OsO_4 oxidation. The ^{1}H NMR spectrum of the diol showed the presence of a carbinylic proton [δ 3.67 (1 H, s, sharpened on D_2O exchange)] while the mass spectrum showed peaks at m/e 75 for a $HOCH_2$—C(CH_3)=OH^+ ion and at m/e 164 for an $M^+ - 74$ ion. On acetylation at room temperature, the diol yielded a monoacetate [δ 5.18 (1 H, s)]. All the above data thus allowed us to conclude that the original sesquiterpene must contain a –C–CH_2–C(CH_3)OH– moiety.

Because of the cooccurrence of ledol (**2**) and ishwarane (**3**), we initially considered structures **4** and **5a** for the sesquiterpene on biogenetic grounds. While 4 was incompatible with the observed multiplicities in the ^{13}C NMR spectrum (vide infra), **5a** could be excluded as follows. Dehydration of this alcohol should have led to **6** and **7** which we prepared from ishwarane via HCl–Et_2O treatment (cf. isomerization of ishwarone).[5] At least the endo olefin obtained from **1** (vide supra) was definitely different (formation of separate crystalline diols on OsO_4 treatment) from *endo*-isoishwarane (**7**) but identical in all respects with the third and a hitherto unreported minor (ca. 1%) product of ishwarane isomerization. The most likely structure for this olefin is therefore **8**. This was further supported by the fact that **9**, the keto alcohol (M^+ 236) obtained by careful Jones oxidation of the derived diol **10**, showed an IR band at 1730 cm^{-1} compatible with a five-membered-ring ketone with an α-hydroxy group. The structure of the sesquiterpene was thus established as **1**.



The stereochemistry at the carbinylic center, which remained to be settled, could however be deduced as *S* since the minor dehydration product (which must necessarily have the structure **11**) after epoxidation to **12** followed by $LiAlH_4$ reduction, afforded **1** as the major component. The stereochemical course of the reaction could be predicted in analogy with the known behavior of the structurally related diterpene, 16-kaurene.[6] Thus, the sesquiterpene must be (12*S*)-7,12-secoishwaran-12-ol (numbering as in ishwarane).

The sesquiterpene could be correlated with ishwarane as follows. Epoxidation of **8** yielded a major product which could be assigned structure **13** (cf. epoxidation of 15-kaurene).[7] Rearrangement of the epoxide with BF_3·Et_2O in benzene was accompanied by a ring expansion, also recorded[8,9] in the kaurane series, leading to a six-membered-ring ketone (ν_{max} 1710 cm^{-1}). Structure **14** for the ketone was corroborated by its identity (TLC, IR) with

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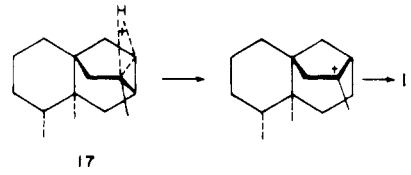
that prepared from *endo*-isoishwarane (7), presumably via the epoxide **15**. Moreover, the CD spectrum of **14**, showed a positive Cotton effect at 291 nm ($\Delta\epsilon$ = +3.56) in conformity with the negative effect in the ORD spectrum[8] of the diterpene ketone **16** bearing a mirror image relationship with **14** around the carbonyl function.

Finally, the above structure for the sesquiterpene was in good agreement with its ^{13}C NMR spectrum. The individual assignments (shown in **1**) have been made by comparison with some known compounds, viz., *ent*-kauran-16α-ol,[10] *ent*-beyerane,[11] cholestane,[12] *trans-anti*-1-methyl decalin,[13] and β-amyrin acetate,[14] using appropriately substituted methyl cyclohexanes[15] as reference compounds.[16,18] As expected, the C_{12} resonance shifted downfield to 91.4 ppm in the spectrum of the acetate while C_8, C_{11}, and C_{12}-methyl signals shifted upfield to 44.8, 47.5, and 19.4 ppm, respectively.[20]

Biogenetically, the sesquiterpene is derivable from the common carbonium ion **17** that might be considered as the immediate precursor to ishwarane.



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Experimental Section

Melting points were determined in open capillaries in a sulfuric acid bath and are uncorrected. Optical rotations were measured in a Hilger-Watts M-511 Microptic photoelectric polarimeter in chloroform solution unless otherwise stated. IR spectra were taken with a Perkin-Elmer Infra-cord (Model 137 or 177) instrument and mass spectra with a Hitachi mass spectrometer (Model RMU-6L). NMR spectra were taken with a Varian CFT-20 instrument and the chemical shift values are expressed in δ (ppm) units with Me_4Si as internal standard. The CD spectrum was recorded with a Roussel-Jouan Dichrograph III. Petroleum ether, bp 60–80 °C, neutral alumina (S. Merck), and silica gel (BDH) were used.

Extraction of the Plant Material. Air-dried roots (5 kg) of the plant were extracted in a Soxhlet apparatus successively with petroleum ether, benzene, chloroform, and alcohol, and the solvents were removed by distillation. The sesquiterpenes were obtained from the petroleum ether extract on repeated chromatography over silica gel.

Isolation of (+)-Ledol (2). (+)-Ledol (300 mg) was eluted with 10–20% benzene in petroleum ether and crystallized from acetonitrile: mp 103–104 °C; $[\alpha]^{25}_D$ +1.9° (*c* 0.98, EtOH); mass spectrum, *m/e* 222 (M^+), 204, 189, 161, 147, 133, 122, 119, 107, 93, 81, 69; IR ν_{max} (Nujol) 3230, 2820, 1450, 1370, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.33 (1 H, dd, *J* = 10, 9 Hz), 0.72 (1 H, ddd, *J* = 12, 9, 6 Hz), 0.94 (3 H, d, *J* = 7 Hz), 0.98 (3 H, s), 1.04 (3 H, s), 1.14 (3 H, s), 1.19–2.08 (11 H, m), 2.13 (1 H, s). The identity was confirmed by direct comparison (mixture melting point, co-TLC, IR) with an authentic sample.

Preparation of Ledglycol from 2. A solution of **2** (100 mg) in pyridine (2 mL) was treated with a few drops of $POCl_3$ and kept overnight, and the reaction mixture was poured over ice–water and extracted with petroleum ether. The organic layer was washed with 2 N HCl and then with aqueous $NaHCO_3$. The major product (40 mg) was separated from the crude mixture by column chromatography over SiO_2–$AgNO_3$. This was dissolved in a mixture of petroleum ether (1 mL), benzene (3 mL), and pyridine (0.4 mL), a benzene solution of OsO_4 (60 mg) was added, and the mixture was kept in the dark for 40 h, H_2S bubbled through the solution, and the mixture was filtered and evaporated. The diol (13 mg) was purified by chromatography: mp 149–150 °C (lit.[22] mp 151.5 °C); $[\alpha]^{25}_D$ -19.4° (*c* 0.62); mass spectrum, *m/e* 238 (M^+), 220, 205, 187, 177, 159; NMR (60 MHz, CCl_4) δ 0.91 (3 H, d, *J* = 6 Hz), 0.96 (3 H, s), 1.00 (3 H, s), 1.15 (3 H, s).

(12*S*)-7,12-Secoishwaran-12-ol (1). The sesquiterpene **1** was eluted with 40% benzene in petroleum ether and crystallized from acetonitrile: mp 150 °C; $[\alpha]^{25}_D$ -20.4° (*c* 0.54); mass spectrum, *m/e* 222 (M^+), 204, 189, 161, 147, 135, 121, 107; IR ν_{max} (Nujol) 3200, 2840, 1450, 1370, 1210, 1160, 1110, 1065 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.73 (3 H, d, *J* = 6 Hz), 0.87 (3 H, s), 1.28 (3 H, s). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.71; H, 12.01.

Acetate of 1. Refluxing 104 mg of **1** for 5 h with pyridine–acetic anhydride followed by column chromatography yielded a crystalline acetate (75% yield): mp 72–73 °C; IR ν_{max} ($CHCl_3$) 2930, 2860, 1710, 1440, 1370, 1265, 1060 cm^{-1}; mass spectrum, *m/e* 204 (M^+ – AcOH), 189, 175, 161, 147, 133, 119, 108, 93, 81, 69, 55, 40.

Dehydration of 1 to 8 and 11. Treatment of **1** (60 mg) with $POCl_3$–pyridine as above followed by separation over SiO_2–$AgNO_3$ gave **8** (28 mg) and **11** (14 mg), both as oils.

The major dehydration product (**8**) had the following physical constants: mass spectrum, *m/e* 204 (M^+), 189, 161, 147, 133, 119, 106; IR ν_{max} ($CHCl_3$) 2890, 1635, 1440, 1180 cm^{-1}; ^1H NMR (CCl_4, 80 MHz) δ 0.70 (3 H, d, *J* = 6 Hz), 0.88 (3 H, s), 1.70 (3 H, d, *J* = 1.8 Hz), 5.63 (1 H, br s).

The minor dehydration product (**11**) had a similar mass spectrum; IR ν_{max} ($CHCl_3$) 2900, 1660, 1460, 1380, 880 cm^{-1}.

Diol 10 from 8. The olefin **8** afforded on OsO_4 treatment as above a diol (57%): mp 140 °C; $[\alpha]^{25}_D$ -42.5° (*c* 0.40); mass spectrum, *m/e* 238 (M^+), 220, 208, 189, 177, 164, 81, 75; IR ν_{max}

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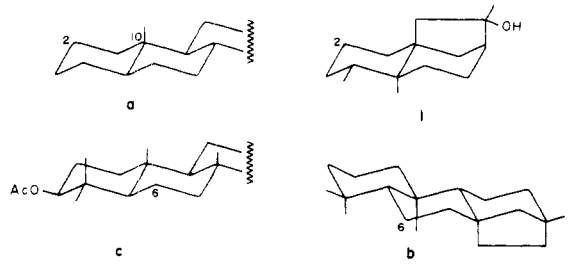
(15) Reference 12, p 64.

(16) The following should be noted. (i) The chemical shift values of C-2 and C-7 may be interchanged, so also those of C-3 and C-6. (ii) Molecular models show that shielding of C-2 by C-11 in **1** should be less than that of C-2 by the methyl carbon in cholestane (a). Appropriate correction for this difference has been made from the chemical shift difference of C-6 in *ent*-beyerane (b) and β-amyrin acetate (c).



(iii) In calculating the δ values for C-5 and C-10 of **1** from those of C-10 of cholestane and C-8 of *ent*-beyerane, respectively, some approximation became necessary in the absence of an exact model. Thus, the difference in δ value of C-2 between 1,1,2-trimethyl- and *trans*-1,2-dimethylcyclohexanes has been taken to represent the shift expected for introducing an axial substituent β to a fully substituted cyclohexane carbon atom. This follows from the success of Beierbeck and Saunders empirical approach[17] ascribing the β-substituent effect to the additional gauche interactions of the new substituents with the hydrogens or alkyl substituents on the concerned carbon.

(17) H. Beierbeck and J. K. Saunders, *Can. J. Chem.*, **53**, 581 (1975).

(18) After submission of the manuscript, our attention has been drawn to a recent paper[19] on the ^{13}C NMR spectra of ishwarane and related compounds. Our assignments in **1**, based on different models, for the carbons 1–4, 9, and 4-methyl are in good accord with those of ishwarane (33.8, 24.1, 31.0, 38.9, 39.4, 16.8 ppm, respectively). The upfield shift of the 5-methyl in our compound by 3.3 ppm due to additional γ_g interaction with C-7 and the difference in the chemical shift values with regard to the carbons in the bridged ring are to be expected.

(19) R. M. Cory and J. B. Stothers, *Org. Magn. Reson*, 11, 252 (1978).

(20) The acetoxy methyl has been assigned the chemical shift of 22.7 ppm by comparison with the value (21.8 ppm) reported[21] for 1-methylcyclopentyl acetate.

(21) M. Christl, H. J. Reich, and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 3463 (1971).

(22) L. Dolejš, O. Moth, M. Souček, V. Herout, and F. Šorm, *Collect. Czech. Chem. Commun.*, **25**, 1483 (1960).

(KCl) 3190, 2920, 2860, 1440, 1360 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 0.77 (3 H, d, J = 6 Hz), 0.88 (3 H, s), 1.28 (3 H, s), 3.67 (1 H, br s).

Monoacetate of 10. Acetylation of **10** (7 mg) with acetic anhydride–pyridine at room temperature overnight afforded the monoacetate (4 mg); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.76 (3 H, d, J = 6 Hz), 0.90 (3 H, s), 2.17 (3 H, s), 5.18 (1 H, s).

Keto Alcohol 9 from 10. Jones oxidation of **10** (2 mg) gave the keto alcohol **9**: mass spectrum, m/e 236 (M^+), 208, 193, 190, 175, 165, 150, 123, 109; IR ν_{max} (Nujol) 3400–3280 (br), 2920, 2860, 1730, 1455, 1380 cm^{-1}.

Acid Isomerization of Ishwarane (3). A solution of **3** (100 mg) in dry ether (5 mL) was saturated with dry HCl gas and kept at room temperature for 2 days. The product was a mixture from which **7** (one of the two major components) was separated (28% yield) by chromatography over SiO_2–$AgNO_3$: mass spectrum, m/e 204 (M^+), 189, 176, 161, 133, 120, 106; IR (neat) ν_{max} 2900, 1660, 1440, 1380, 1050 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 0.70 (3 H, d, J = 6 Hz), 0.87 (3 H, s), 1.70 (3 H, d, J = 2 Hz), 5.62 (1 H, s).

The minor acid-isomerization product, which was found to be identical with **8**, was obtained from the same chromatography in 1% yield.

Diol 5b from endo-Isoishwarane (7). Treatment with OsO_4, as above, of **7** gave (43%) a crystalline diol: mp 172–174 °C; $[\alpha]^{25}_D$ −140.9° (c 0.44); mass spectrum, m/e 238 (M^+), 223, 220, 208, 205, 202, 189, 177, 162, 147, 135; IR ν_{max}(KCl) 3230, 2940, 2860, 1450, 1380, 1320, 1065 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 0.78 (3 H, d, J = 6 Hz), 0.93 (3 H, s), 1.28 (3 H, s), 2.4–2.6 (2 H, br s), 3.75 (1 H, s).

Keto Alcohol from *endo*-Isoishwarane (7)-Diol. Jones oxidation of the diol, mp 172–174 °C, afforded in 50% yield the keto alcohol: mass spectrum, m/e 236 (M^+), 218, 208, 190, 175, 165, 136, 123, 109; IR ν_{max} (Nujol) 3340, 2925, 2860, 1715, 1460, 1375 cm^{-1}.

Epoxidation of 11 to 12. Treatment of a $CHCl_3$ solution of **11** (20 mg) with a $CHCl_3$ solution of perbenzoic acid at 0 °C for 1 h followed by usual workup and chromatography over neutral alumina yielded **12** (12 mg); IR (neat) ν_{max} 2930, 2860, 1450, 1385 cm^{-1}.

Reduction of 12 to 1. The epoxide (12 mg) was reduced with an excess of $LiAlH_4$ in ether (10 mL) at room temperature for 27 h. Usual workup followed by chromatographic purification afforded the predominant product (6 mg) which was found to be identical (melting point, mixture melting point, TLC, $[\alpha]_D$, IR) with **1**.

Epoxidation of 8 to 13. Treatment of **8** (40 mg) with a $CHCl_3$ solution (5 mL) of perbenzoic acid at 0 °C for 1 h, usual workup, and subsequent chromatography over neutral alumina yielded **13** (22 mg): mp 46–48 °C; mass spectrum, m/e 220 (M^+), 205, 191, 177, 163, 151, 135, 121, 109, 107, 95, 93, 91, 81, 71; IR (neat) ν_{max} 1070, 1020, 900, 845 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 0.77 (3 H, d, J = 6 Hz), 0.85 (3 H, s), 1.35 (3 H, s), 3.17 (1 H, s).

Isomerization of 13 to 14. A drop (0.02 mL) of freshly distilled BF_3·Et_2O was added to **13** (20 mg) in dry benzene (2 mL) and left at 20 °C for 15 min. Usual workup and chromatography yielded **14** (15 mg): mass spectrum, m/e 220 (M^+), 202, 192, 191, 177, 163, 162, 147, 135, 123, 109, 107, 95, 93, 91, 81, 79; IR (neat) ν_{max} 1710, 1440, 1327, 1103, 1083, 910 cm^{-1}; CD (MeOH) λ_{max} 291 nm ($\Delta\epsilon$ = +3.56).

Conversion of 7 to 14. An ether solution (3 mL) of monoperphthalic acid was added to 69 mg of **7** and the mixture was left at 0 °C for 5 h and worked up in the usual manner. Chromatographic purification yielded **14** (25 mg), identified from TLC and IR.

Acknowledgment. We are grateful to Professor (Mrs.) A. Chatterjee, Calcutta University, Professor U. R. Ghatak, IACS, Calcutta, the Bangalore NMR facility, and M/S. JEOL Ltd., Tokyo, for the NMR spectra, to Dr. S. P. Popli, CDRI, Lucknow, for the CD spectrum, and to Professor V. Herout of the Czechoslovak Academy of Sciences, Prague, and Drs. K. Nagarajan and P. C. Parthasarathy of the CIBA-Geigy Research Centre, Bombay, for some authentic specimens. One of us (S. C.) thanks the NCERT, New Delhi, for a fellowship.

Registry No. **1**, 74912-09-7; **1** acetate, 74912-10-0; **2**, 577-27-5; **3**, 26620-70-2; **5b**, 74912-17-7; **5b** keto alcohol, 74912-18-8; **7**, 22471-63-2; **8**, 74929-66-1; **9**, 74912-11-1; **10**, 74912-12-2; **10** monoacetate, 74958-41-1; **11**, 74912-13-3; **12**, 74912-14-4; **13**, 74912-15-5; **14**, 74912-16-6.

Thermochemical Behavior of *o*-Azidocinnamonitriles

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Ring-closed products have been reported from heat treatment of aryl azides that have unsaturated ortho substituents.[1-6] We wished to study the thermal reactions of *o*-azidocinnamonitriles to determine whether the azido group, or its intermediate nitrene, would attack the C=C unsaturation or the CN group. In addition, this system offered the opportunity to determine the effect of the two different geometrical arrangements around the double bond on the course of the cyclization. Accordingly, we have synthesized compounds **2a–c** and **6a–c** and have examined their thermal reactions.

Results and Discussion

The aryl azides were obtained as analytically pure, crystalline compounds from the corresponding anilines by diazotization and treatment with sodium azide (see Table I). Preparation of the intemediate *o*-aminocinnamonitriles **1** and **5** and the assignment of their configurations are described below.

Reaction of *o*-nitrobenzaldehyde with diethyl cyanomethylphosphonate[7] gave principally (*Z*)-*o*-nitrocinnamonitrile, with a small amount of the *E* isomer, from which it was separated by chromatography. Hydrogenation of the *Z* isomer gave **1a** (see Chart I) contaminated with a little 3-(2-aminophenyl)propionitrile. This mixture was used in the subsequent diazotization reaction, from which **2a** was isolated by chromatography. The facile conversion of **1a** to **4a** has interfered with previous attempts to obtain it.[8] The methyl analogue **1c** was also made by hydrogenation of the corresponding nitrocinnamonitrile, while **1b** was prepared by thermal decomposition of 7-chloro-5-phenyl-1*H*-1,2-benzodiazepine-3-carboxylic acid.[9] Compounds **5a–c** were made by reaction of the corresponding *o*-aminoaryl carbonyl compounds with diethyl cyanomethylphosphonate.[7]

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