showed a single ninhydrin-positive spot. A small portion of the aqueous phase was evaporated and subjected to standard derivatization procedures[17] to give the trifluoroacetyl *n*-butyl esters of any amino acids present. Analysis by GC/MS indicated the presence of *N*-(trifluoroacetyl)valine *n*-butyl ester (**2**). TLC analysis of the underivatized hydrolyzate on Chiralplates (Macherey-Nagel) and comparison with authentic standards indicated that the valine obtained from hydrolysis of brassicicolin A was racemic.

Basic Hydrolysis of 6. A sample of brassicicolin A (10 mg) was dissolved in 3 mL of methanol to which 10 mg of Na_2CO_3 was added. The mixture was allowed to stir at room temperature for 24 h and was then evaporated, dissolved in 3 mL of water, and extracted with dichloromethane (3 × 5 mL). The aqueous phase was collected and evaporated to give a white residue, which was taken on to the next step without further purification.

Acetylation of Basic Hydrolysis Product. The residue obtained after basic hydrolysis as described above was suspended in 3 mL of pyridine to which 0.5 mL of acetic anhydride was added. The mixture was allowed to stir for 18 h and was subsequently evaporated, dissolved in water, and extracted with dichloromethane (3 × 5 mL). The organic phase was dried ($MgSO_4$) and evaporated to afford 4.2 mg (67% yield) of hexaacetyl-D-mannitol (**3**). The structure and stereochemistry of this product were assigned by comparison to an authentic standard prepared by acetylation of D-mannitol under identical conditions (GC/MS, HRMS, ^{1}H NMR, $[\alpha]_D$).

Selective Hydrolysis of the Isocyanide Groups. A small amount (2.0 mg) of brassicicolin A was dissolved in 1 mL of methanol. Three drops of acetic acid were added, and the solution was allowed to stand at room temperature overnight. Evaporation of the solvent and analysis by IR and ^{1}H NMR demonstrated the absence of isocyanide groups (no IR band at 2150 cm^{-1}; no C*H*NC proton NMR multiplet at 4.05 ppm), and the presence of formamide groups [broad new IR absorption at 1660 cm^{-1}; new ^{1}H NMR signals at 6.30–6.35 (N*H*CHO), 8.20–8.25 (NHC*H*O), and 4.60–4.65 ppm (C*H*NHCHO)].

Reductive Deisocyanation of 6. A sample of brassicicolin A (38 mg, 0.056 mmol) and a catalytic amount of AIBN (0.1 mg) were dissolved in 15 mL of anhydrous benzene under a nitrogen atmosphere, and 32.6 mg (0.112 mmol) of tri-*n*-butyltin hydride was added via syringe.[8] After stirring for 8 h at 80 °C, the solution was cooled, evaporated to dryness, and chromatographed on a small column of silica gel (1 × 5 cm) using a stepwise gradient from hexane to ethyl acetate. Fractions collected at 20% ethyl acetate were pooled to give 11 mg (31% isolated yield) of the white crystalline symmetrical reduction product **5**. Compound **5** has the following properties: R_f 0.71 (9:1 chloroform–methanol); mp 50–51 °C; $[\alpha]_D$ +23.0° (*c* 1.10, CH_2Cl_2); IR (neat) 3517, 2962, 2934, 2875, 1743 (br), 1468, 1371, 1293, 1210, 1032, 983 cm^{-1}; EIMS (30 eV) major ions at *m/z* 634 (M^+, 2.1), 574 (19), 518 (32), 475 (23), 417 (100), 358 (12), 318 (12), 299 (12), 257 (35), 185 (49), 157 (35), 115 (13), 85 (39), 57 (9.7); FABMS (thioglycerol) major ions at *m/z* 635 (M + H, 7.8%), 617 (5.9), 575 (18), 533 (5.3), 517 (16), 475 (16), 428 (34), 417 (3.4), 333 (3.5), 291 (4.7), 85 (42), 57 (40); ^{1}H NMR ($CDCl_3$), see Table I; ^{13}C NMR ($CDCl_3$), see Table I; HRFABMS obsd 635.3316, calcd for $C_{30}H_{50}O_{14}$ + H 635.3278. Anal. Calcd for $C_{30}H_{50}O_{14}$: C, 56.78; H, 7.94. Found: C, 56.78; H, 7.65.

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Conversion of Dehydroabietic Acid into 20-Keto-*C*-aryl-18-norsteroids. Formation of the D Ring

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Dehydroabietic acid (**1a**) has been converted into 17-epimeric 20-keto-*C*-aryl-18-norsteroids **13** via a sequence of trasformations involving as key step the regioselective functionalization of the 13-isopropyl group of **1a**.

The preparation of ring C aromatic steroids has attracted the attention of many workers due to their interesting pharmacological properties. In recent years several *C*-aryl-18-norsteroids have been totally synthesized[1] or prepared from different resin acids[2] and by conversion of naturally ocurring steroids to the C-aromatic system.[3]

In this paper we describe the elaboration of the five-membered D ring of a 20-keto-*C*-aryl-18-norsteroid from readily available dehydroabietic acid (**1a**), which with its aromatic ring C and C-13 isopropyl side chain has shown to be a suitable starting material for the preparation of 15- and 17-keto-18-norsteroids.[4a,b] The synthetic route used to prepare this ring C-aromatic steroid system is outlined in Schemes I and II.

The main synthetic problem associated with the use of this resin acid as the starting material for the preparation of C-aromatic steroids is the regioselective functionalization of the C-13 isopropyl group; the use of oxidizing agents such as CrO_3,[5a] $KMnO_4$,[5b] SeO_2,[5c] or NBS[5d] results in the oxidation of both activated benzylic positions or in the

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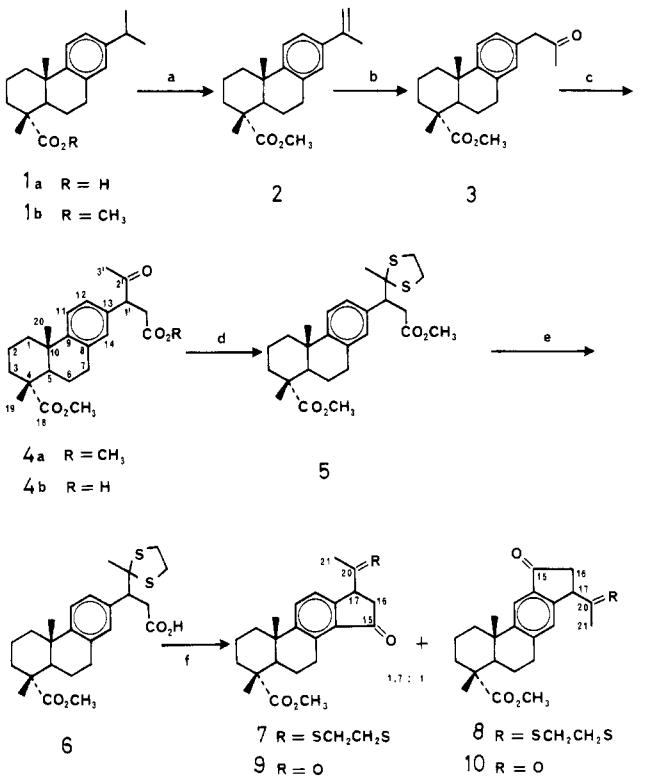
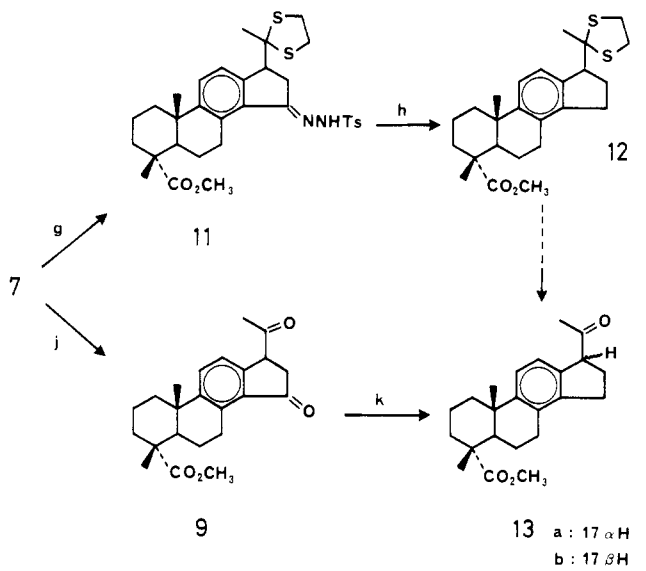
Scheme I[a]



[a] (a) DDQ, C_6H_6, ref; (b) TTN, CH_3OH, 56% from **1b**; (c) KH, THF, then BEt_3, then $BrCH_2CO_2CH_3$, 83%; (d) $HSCH_2CH_2SH$, BF_3 etherate, CH_2Cl_2, 91%; (e) NaOH, EtOH, 50 °C, 97%; (f) polyphosphoric acid, P_2O_5, 40 °C, 67%.

Scheme II[a]



[a] (g) $TsNHNH_2$, C_6H_6, BF_3 etherate, 96%; (h) catecholborane, $CHCl_3$, then NaOAc ref, 20%; (j) TTN, CH_3OH–THF, 80%; (k) H_2, Pd/C, AcOH, 80%.

preferential oxidation of the C-7 position. We have found that the use of 2,3-dichloro-5,6-dicyanoquinone (DDQ) as the dehydrogenation agent allows the regioselective functionalization of the isopropyl group (Scheme I). Thus, heating a solution of methyl dehydroabietate (**1b**) and DDQ under reflux in dry benzene gave after workup (see Experimental Section) a mixture, inseparable by column chromatography, of starting material **1b** (52%) and methyl abieta-8,11,13,15-tetraen-18-oate (**2**) (45%) together with a small amount of methyl abieta-6,8,11,13-tetraen-18-oate (less than 3%) according to GC analysis of the product mixture.[6] Attempts to improve the yield of olefin **2** by increasing the amount of DDQ used or the reaction time resulted only in substantial material losses. Although the yield of desired alkene **2** is only moderate the fact that unconsumed methyl dehydroabietate **1b** is recovered in the next step (see below) and may be efficiently recycled makes this reaction a useful method for the regioselective functionalization of the C-13 isopropyl group. This group was conveniently modified in readiness for the formation of the D ring in the next step. Thus, treatment of the reaction mixture obtained from exposure of methyl dehydroabietate (**1b**) to DDQ with thallium(III) nitrate (TTN)[7] in methanol at room temperature allowed the isolation of methyl ketone **3** after chromatographic separation from unchanged methyl dehydroabietate (**1b**) in an overall yield (two steps) of 56% based on recovered **1b**.

Alkylation of ketone **3** was accomplished by successive treatment of its thermodynamic potassium enolate with triethylborane and methyl bromoacetate. This alkylation via the potassium enoxyborate[8] proceeded with high regioselectivity and produced neither polyalkylation nor O-alkylation products, in contrast to the alkylation of the free enolate which took place in low yield. Although, the ^1H and ^{13}C NMR spectra of **4a** seemed to indicate a single diastereomer its diastereomeric nature was shown by the spectroscopic data of protected ketone **5** (vide infra).

Since initial attempts at direct cyclization of keto acid **4b** (derived from keto ester **4a** by partial hydrolysis with NaOH–EtOH–H_2O) were not fruitful[9] we decided to protect the ketone carbonyl group of **4a** as its ethylene thioketal. Thus, treatment of **4a** with 1,2-ethanedithiol and boron trifluoride etherate and subsequent chromatography afforded thioketal **5** in high yield. The ^{13}C NMR spectrum of this material comfirmed the presence of both epimers at C-1′; there is one peak for each carbon atom in the proton noise decoupled spectrum with exception of C-12 and C-14 carbon atoms which appear as two doublets of the same intensity at 126.15/126.00 and 129.35/129.20 ppm.

In order to form the D ring by using an intramolecular Friedel–Crafts acylation the diester **5** was converted to the half-ester **6** by partial hydrolysis with alcoholic NaOH. The planned subsequent intramolecular Friedel–Crafts acylation presented some difficulties. We first attempted the cyclization reaction via the corresponding acid chloride ($SOCl_2$, pyridine or AcCl in situ) with $AlCl_3$ (CS_2 or C_6H_6 as solvents), but no cyclized product was obtained from the reaction mixtures. Fortunately, cyclized products **7** and **8** were isolated when the intramolecular acylation was carried out in polyphosphoric acid under carefully controlled conditions, especially with regard to temperature. We believe that the failure to observe any cyclized product in the initially attempted conditions may result from the intolerance of the thioketal moiety to the reaction conditions. It is also of note that about 5% of deprotected cyclized products **9** and **10** were obtained from the poly-

(6) Compound **2** and methyl abieta-6,8,11,13-tetraen-18-oate were prepared through independent routes to be used as reference compounds in the GC analysis. The former was prepared from methyl dehydroabietate (**1b**) as described at the end of the Experimental Section and the latter from methyl abietate as described in: Dupont, G.; Dulou, R.; Ourisson, G.; Thibault, C. *Bull. Soc. Chem. Fr.* **1955**, 708.

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(9) From the complex reaction mixtures obtained the γ-lactone derived from lactonization through the enolic form of the 2′-carbonyl group was the only identifiable product.

phosphoric acid cyclization reaction mixture. Integration of the aromatic signals in the ^1H NMR spectrum of the crude cyclization mixture revealed a ratio of 1.7:1 of the cyclized products **7** and **8**. Formation of the major product **7** is in agreement with previous observations.[10] Although **7** and **8** have similar R_f values they could be separated by careful flash chromatography in 43% and 24% yields, respectively.

Transformation of the tetracyclic ketone **7** into the target 20-keto-*C*-aryl-18-norsteroid **13** required removal of the C-15 carbonyl group and unmasking of the C-17 acetyl function (Scheme II). Toward this end, a solution of **7** in benzene was treated with tosylhydrazine and a catalytic amount of boron trifluoride etherate, which generated an almost quantitative yield of crystalline tosylhydrazone **11**. Reduction of **11** with catecholborane under standard conditions[11] appeared to proceed smoothly when monitored by TLC but a disappointingly low yield (less than 20%) of reduced compound **12** was obtained after workup and chromatography; no other compound was isolated from the crude reaction mixture. The reasons for the low yield obtained in this reaction are not immediately apparent, though the instability of **12** may be partially responsible.[12] Although compound **12** could have been transformed into **13**, the low yield obtained in the reduction step prompted us to investigate an alternative strategy for the conversion of **7** to **13**. Cleavage of the protecting group in **7** (TTN in methanol–tetrahydrofuran) afforded solid diketone **9** in 80% isolated yield.[13] The aromatic ^1H NMR region shows the characteristic AB pattern for the two aromatic protons and it is of note that the corresponding signals for the methyl hydrogens of the $COCH_3$ groups of both epimers of **9** at C-17 appear as two singlets of similar intensity at well-differentiated δ (2.22 and 2.17 ppm).

Finally, hydrogenolysis of diketone **9** over Pd–C or PtO_2 in acetic acid gave the 17-epimeric mixture **13**. Partial reduction of the C-17 acetyl group took place during the hydrogenolysis reaction, but treatment of the crude reaction mixture with Jones reagent gave, after workup and chromatography, a 1:1 mixture of 17αH and 17βH **13**, the separation of which was achieved by preparative high-pressure liquid cromatography (HPLC). The stereochemistry at C-17 of compounds **13a** and **13b** was established by comparison of ^1H and ^{13}C NMR data of both isomers with those of analogous structures.[3,14] In particular, the acetyl protons of the 17αH isomer **13a** resonate at a slightly lower field than those of the 17βH isomer **13b** (2.17 and 2.14 ppm, respectively). Although the ^{13}C NMR spectra of both isomers are essentially identical, they differ significantly in the shielding of C-21; this carbon resonates at 0.22 ppm upfield in the 17βH isomer **13b** compared with the 17αH isomer **13a** (27.58 and 27.80 ppm, respectively). This shielding of C-21 in the 17βH isomers has been attributed[14] to a higher degree of γ-gauche interaction with C-16. The coupling constants of the 17H protons with the 16αH and 16βH protons in both isomers ($J_{17\alpha,16\alpha}$ = 5.9 Hz and $J_{17\alpha,16\beta}$ = 7.9 Hz for **13a** and $J_{17\beta,16\alpha} = J_{17\beta,16\beta}$ = 7 Hz for **13b** are in reasonable agreement with a five-membered D ring as a C-16 β-envelope.[15] This conformation also accounts for the difference in the NMR shift of the 12H protons induced by tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octadionato)europiium(III) [Eu(fod)$_3$]. When 1 equiv or more of the shift reagent was added, the signals due to each aromatic proton were clearly resolved as two doublets, but while the shift reagent causes the same deshielding in the 11H protons of both isomers, the deshielding in the 12H protons is greater for the 17αH isomer **13a** than for the 17βH isomer **13b**, indicating a shorter C-20 oxygen to 12H proton distance for **13a** than for 13b as is shown by Drieding models of both isomers.

Experimental Section

Melting points were determined on a Kofler apparatus and are uncorrected. IR spectra were recorded as liquid films for oils and in KBr disks for solids in a Perkin-Elmer Model 281 spectrophotometer. The ^1H and ^{13}C NMR spectra were measured at 200.13 and 50.32 MHz, respectively (Bruker AC-200 model) in $CDCl_3$ solution (room temperature); chemical shifts are reported in ppm (δ) relative to Me_4Si as an internal standard. The carbon type (methine, methylene, methyl, or quaternary) was determined by DEPT experiments. Mass spectra were run by electron impact (70 eV) on a Varian MAT-311A spectrometer. Elemental analyses were performed by Servicio de Semimicroanalisis del CSIC (Barcelona). Optical rotations were measured with a Perkin-Elmer 141 polarimeter. Gas chromatography was carried out on a Perkin-Elmer Model 3920B, using helium as carrier gas and a Minigrator to integrate peak areas. Thin-layer chromatography was carried out on Merk 0.25 mm silica gel 60 HF_{254} analytical aluminium plates. Column chromatography separations were performed on silica gel (Merk silica gel 60, 230–400 mesh).

Commercially available chemicals were used as obtained without further purification, except for solvents, which were purified and dried before use by standard methods. Dehydroabietic acid (**1a**) was obtained from commercial colophony following the procedure of Halbrook.[16] Its methyl ester (**1b**) was prepared by reaction of its lithium salt with dimethyl sulfate in DMF.[17]

Reaction of Methyl Dehydroabietate (1b) with DDQ. A solution of **1b** (10.0 g, 31.84 mmol) and DDQ (8.0 g, 35.24 mmol, 1.1 equiv) in dry benzene (700 mL) was heated under reflux with stirring for 2.5 h. The reaction mixture was cooled to room temperature and was filtered to recover the 2,3-dichloro-5,6-dicyanohydroquinone formed (5.70 g). Concentration of the filtrate gave an oily residue, which was dissolved in hexane, filtered, and then concentrated. The residue was chromatographed on a short silica gel column with hexane–ether (9:1) as eluent to give a nearly colorless oil (7.90 g, 79%). GC analysis ($^1/_8$-in. diameter, 2-m column packed with 5% EGA on Chromosorb W AW; 250 °C injector and detector temperature, 210 °C column temperature; flow rate, 35 mL/min) indicated that this contained two major components with retention times of 13.4 and 15.2 min, corresponding to unreacted methyl dehydroabietate (**1b**) (52%) and methyl abieta-8,11,13,15-tetraen-18-oate (**2**) (45%) together with a small amount (2%) of a third component (retention time 24 min) corresponding to methyl abieta-6,8,11,13-tetraen-18-oate.

Methyl 13-(2′-Oxopropyl)podocarpa-8,11,13-trien-18-oate (3). To a solution of the mixture of **1b** and **2** (6.20 g, containing 2.79 g of 2, 8.94 mmol) in MeOH (114 mL) was added Tl(ON-

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(12) The instability of all tetracyclic products obtained in this work was a continuous problem in their handling. All of them were changed when left standing at room temperature, giving extensive decomposition, and a striking sensitivity to the acid medium was shown by some of them (e.g., incomplete elimination of acid during workup of the cyclization reaction produced extensive decomposition of the cyclized products, most of the products formed being apparently polymeric). Only solid tetracyclic compounds were stable for long periods of time, if kept in the refrigerator under argon.

(13) Since separation of cyclized products **7** and **8** proved to be difficult we found it more convenient to deprotect the crude mixture from the cyclization reaction and to separate the deprotected cyclized products **9** and **10**. A better yield of diketone **9** was obtained in this way (see Experimental Section).

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(15) This conformation has been found for other C-aryl-18-norsteroids and closely related molecules. See ref 3 and Ferguson, G.; Parvez, M.; Watson, R. T.; Cheung, H. T. A. *J. Chem. Res. Synop.* **1983**, 278; *J. Chem. Res. Miniprint* **1983**, 2539.

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$O_2)_3 \cdot 3H_2O$ (3.98 g, 8.96 mmol) with stirring at room temperature. After 30 min, water was added, and the crystals were filtered off. The filtrate was extracted with ether, which was washed with saturated $NaHCO_3$ solution and brine. After drying over sodium sulfate, the solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography on silica gel to give unreacted **1b** (3.1 g, hexane–ether (9:1) as eluent) and **3** (2.9 g, 99% based on **2**, hexane–ether (7:3) as eluent) as an oil: $[\alpha]^{22}_D$ +46.9° (*c* 0.75, $CHCl_3$); IR 1710–1730 (ester and ketone), 1610, 1500 cm^{-1} (Ar ring); ^1H NMR δ 7.20 (d, J = 8.1 Hz, 1 H, H-11), 6.95 (dd, J = 8.1 and 1.4 Hz, 1 H, H-12), 6.87 (br s, 1 H, H-14), 3.66 (s, 3 H, CO_2CH_3), 3.61 (s, 2 H, $ArCH_2CO$), 2.88 (m, 2 H, H-7α,β), 2.27 (m, 1 H, H-1β), 2.22 (dd, J = 12.5 and 2.0 Hz, 1 H, H-5α), 2.15 (s, 3 H, CH_3CO), 1.27 and 1.20 (each s, 3 H, 2 × CH_3); ^{13}C NMR δ 206.67 (C), 178.96 (C), 148.29 (C), 135.40 (C), 131.11 (C), 129.86 (CH), 126.73 (CH) 124.63 (CH), 51.86 (CH_3), 50.48 (CH_2), 47.57 (C), 44.72 (CH), 37.89 (CH_2), 37.00 (CH_2), 36.60 (C), 29.76 (CH_2), 29.22 (CH_3), 24.99 (CH_3), 21.50 (CH_2), 18.48 (CH_2), and 16.45 (CH_3); MS, m/e (relative intensity) 328 (M^+, 13.1), 313 (15.5), 285 (4.8), 254 (19.5), 253 (100), and 225 (12.6); HRMS, calcd for $C_{21}H_{28}O_3$ 328.2038, found, 328.2057.

Methyl 13-[1′-((Methoxycarbonyl)methyl)-2′-oxopropyl]podocarpa-8,11,13-trien-18-oate (4a). To a stirred suspension of prewashed potassium hydride (0.679 g of a 30.7% mineral oil dispersion of KH, 5.197 mmol) in freshly distilled THF (15 mL) at 0 °C under argon was added, dropwise via syringe, ketone **3** (1.623 g, 4.948 mmol) in THF (5 mL). After hydrogen evolution had ceased (ca. 1 h at 0 °C) the orange mixture was stirred at room temperature for a further 30 min, at which time 6.4 mL (6.4 mmol) of a 1 M solution of triethylborane in THF was added to the mixture. After 10 min methyl bromoacetate (2.5 mL, 24.75 mmol, 5 equiv) was added in one portion. A white precipitate appeared and the pale yellow heterogeneous mixture was stirred for 12 h at room temperature. The reaction was quenched with saturated aqueous ammonium chloride solution until no more effervescence could be detected. Water was added and the aqueous layer extracted with ether. The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure followed by chromatography of the residue (gradient elution, 20% to 40% hexane–ether) gave recovered methyl bromoacetate (2.7 g), unreacted **3** (0.249 g), and an inseparable 1:1 mixture (see Discussion section) of the C-1′ epimers of **4a** (1.35 g, 83% based on consumed **3**): IR 1730 (ester), 1715 (ketone), 1612, 1500 cm^{-1} (Ar ring); ^1H NMR δ 7.13 (d, J = 8.6 Hz, 1 H, H-11), 6.89 (d, J = 8.6 Hz, 1 H, H-12), 6.79 (br s, 1 H, H-14), 4.06 (dd, J = 10.05 and 4.6 Hz, 1 H, ArCHCO), 3.59, 3.61 (each s, 3 H, 2 × CO_2CH_3), 3.12 (dd, J = 17.0 and 10.05 Hz, 1 H, $CHCO_2$), 2.80 (m, 2 H, H-7α,β), 2.42 (dd, J = 17.0 and 4.6 Hz, 1 H, $CHCO_2$, 2.22 (m, 1 H, H-1β), 2.13 (dd, J = 12.7 and 2.0 Hz, 1 H, H-5α), 2.05 (s, 3 H, CH_3CO), 1.22 and 1.14 (each s, 3 H, 2 × CH_3) [irradiation at δ 4.06 collapsed the doublets of doublets at δ 3.12 and 2.42 to doublets (J = 17 Hz)]; ^{13}C NMR δ 206.85 (C), 178.76 (C), 172.48 (C), 148.89 (C), 135.71 (C), 134.09 (C), 128.47 (CH), 125.39 (CH), 124.90 (CH), 54.12 (CH), 51.78 (CH_3), 51.55 (CH_3), 47.45 (C), 44.60 (CH), 37.76 (CH_2) 36.94 (C), 36.55 (CH_2), 36.50 (CH_2), 29.68 (CH_2), 28.78 (CH_3), 24.87 (CH_3), 21.36 (CH_2), 18.36 (CH_2), and 16.36 (CH_3); MS, m/e (relative intensity) 401 (3.5), 400 (M^+, 12.9), 385 (1.2), 357 (29.8), 325 (5.5), 316 (12.1), 315 (56.3), 297 (3.2), and 43 (100); HRMS, calcd for $C_{24}H_{32}O_5$ 400.2250, found 400.2261.

Methyl 13-[1′-((Methoxycarbonyl)methyl)-2′,2′-(ethylenedithio)propyl]podocarpa-8,11,13-trien-18-oate (5). To a stirred solution of ketone **4a** (0.948 g, 2.370 mmol) in dry CH_2Cl_2 (29 mL) at room temperature under argon was added, via syringe, 1,2-ethanedithiol (0.500 mL, 5.95 mmol, 2.5 equiv) followed by ethereal boron trifluoride etherate (0.192 mL). The mixture was stirred at room temperture for 24 h and then hydrolyzed with 12.5 mL of 5% aqueous NaOH. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with 5% NaOH solution and brine. After drying and concentration the residue was chromatographed on silica gel (hexane–ether, 8:2) to give **5** (1.026 g, 91%) as a solid: mp 128–131°C (from ethanol); IR 1730 (ester), 1500 cm^{-1} (Ar ring); ^1H NMR δ 6.9–7.1 (m, 3 H, Ar protons), 3.64 (s, 3 H, CO_2CH_3), 3.52 (s overlapped with dd, 4 H, CO_2CH_3 and H-1′), 3.4–3.2 (dd overlapped with m, 5 H, $CHCO_2$ and 2 × SCH_2), 2.93 (dd, J = 9.8 and 15.9 Hz, 1 H, $CHCO_2$), 2.85 (m partially overlapped with dd at 2.93, 2 H, H-7α,β), 1.60 (s, 3 H, CH_3CS_2), 1.25 and 1.15 (each s, 3 H, 2 × CH_3); ^{13}C NMR δ 178.72 (C), 172.60 (C), 148.10 (C), 137.11 (C), 134.12 (C), 129.35 and 129.20 (CH), 126.15 and 126.00 (CH), 123.52 (CH), 70.91 (C), 52.12 (CH), 51.65 (CH_3), 51.26 (CH_3), 47.40 (C), 44.60 (CH), 40.35 (CH_2), 39.58 (CH_2), 38.21 (CH_2), 37.68 (CH_2), 36.78 (C), 36.43 (CH_2), 33.29 (CH_3), 29.74 (CH_2), 24.84 (CH_3), 21.42 (CH_2), 18.34 (CH_2), and 16.30 (CH_3); MS, m/e (relative intensity) 476 (0.45, M^+), 445 (0.4), 357 (0.2), and 119 (100). Anal. Calcd for $C_{26}H_{36}O_4S_2$: C, 65.51; H, 7.61. Found: C, 65.21; H, 8.01.

Methyl 13-[1′-(Carboxymethyl)-2′,2′-(ethylenedithio)propyl]podocarpa-8,11,13-trien-18-oate (6). To a suspension of diester **5** (1.024 g, 2.151 mmol) in ethanol (20 mL) was added 2% alcoholic NaOH (26 mL, 13.0 mmol, 6 equiv) and the mixture stirred for 3 h at 50 °C. The reaction mixture was cooled to room temperature, water was added, and the mixture was acidified with 2 N HCl and extracted with ether. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave pure **6** (0.961 g, 97%) as a solid: mp 87–89 °C; IR 3660–2300 (acid), 1740–1710 (ester and acid), 1500 cm^{-1} (Ar ring); ^1H NMR δ 6.9–7.1 (m, 3 H, Ar protons), 3.63 (s, 3 H, CO_2CH_3), 3.47 (dd, J = 9.55 and 4.0 Hz, 1 H, H-1′), 3.36–3.15 (dd partially overlapped with m, 5 H, $CHCO_2$ and 2 × SCH_2), 2.93 (dd, J = 16.5 and 9.55 Hz, 1 H, $CHCO_2$), 2.83 (m, 2 H, H-7α,β), 1.57 (s, 3 H, CH_3CS_2), 1.24 and 1.15 (each s, 3 H, 2 × CH_3); ^{13}C NMR δ 179.07 (C), 178.30 (C), 148.40 (C), 137.03 (C), 134.40 (C), 129.49 and 129.25 (CH), 126.42 and 126.15 (CH), 123.78 (CH), 71.14 (C), 51.87 (CH + CH_3), 47.61 (C), 44.72 (CH), 40.49 (CH_2), 39.77 (CH_2), 38.33 (CH_2), 37.80 (CH_2), 36.97 (C), 36.55 (CH_2), 33.46 (CH_3), 29.91 (CH_2), 25.01 (CH_3), 21.56 (CH_2), 18.49 (CH_2), and 16.45 (CH_3).

Cyclization Reaction of 5b. 4α-Carbomethoxy-20,20-(ethylenedithio)-4β-methyl-18-nor-5α-pregna-8,11,13-trien-15-one (7) and Isomer 8. An intimate mixture of powdered half ester **6** (0.300 g, 0.649 mmol), polyphosphoric acid (8.0 g), and P_2O_5 (0.800 g) was mechanically stirred at 40 °C for 7 h. After cooling, the brown-orange reaction mixture was quickly poured into 150 mL of an ice-cold aqueous solution of Na_2CO_3 and extracted with ether. The extract was washed with saturated Na_2CO_3 solution and brine and was filtered through a pad of basic alumina. Evaporation of the ether gave a crude mixture of cyclized products **7** and **8** in a ratio 1.7:1 (^1H NMR analysis) as a semisolid (0.273 g). The two isomers were separated by careful flash chromatography with hexane–ether (8:2) as eluent.

7: 0.125 g (43%); mp 186–187 °C (from hexane); IR 1730 (ester), 1710 (ketone), 1575, and 1600 cm^{-1} (Ar ring); ^1H NMR δ 7.73 (d, J = 8.3 Hz, 1 H, H-12), 7.45 (d, J = 8.3 Hz, 1 H, H-11), 3.85 (dd, J = 7.6 and 2.5 Hz, 1 H, H-17), 3.66 and 3.65 (each s, 1.5 H, CO_2CH_3 for the *R* and *S* epimers at C-17), 3.55–2.97 (m, 6 H, 2 × CH_2CS + H-7α,β), 2.86 and 2.84 (two dd, J = 18.9 and 7.6 Hz, 1 H, H-16 of *R*,*S* epimers at C-17), 2.63 (dd, J = 18.9 and 2.5 Hz, 1 H, H-16), 1.59 and 1.58 (each s, 3 H, CH_3CS_2 of *R*,*S* epimers at C-17), 1.25 and 1.20 (each s, 3 H, 2 × CH_3) [irradiation at δ 3.85 caused the doublets of doublets at δ 2.86 and 2.63 to collapse to doublets (J = 18.9 Hz)]; ^{13}C NMR δ 206.03 (C), 178.83 (C), 152.97 (C), 150.13 and 149.99 (C), 136.13 (C), 134.99 (C), 130.21 and 130.05 (CH), 124.65 (CH), 70.55 (C), 51.98 (CH_3), 49.90 (CH), 47.53 (C), 44.75 (CH_2), 44.31 and 44.20 (CH), 40.25 (CH_2), 39.72 (CH_2), 38.29 and 38.20 (CH_2), 37.39 (C), 36.41 (CH_2), 29.80 and 29.68 (CH_3), 27.17 and 26.88 (CH_2), 25.04 (CH_3), 20.88 (CH_2), 18.50 (CH_2), and 16.43 (CH_3); MS, m/e (relative intensity) 446 (0.26, M^+ + 2), 445 (0.6, M^+ + 1), 444 (0.7, M^+), 385 (0.8), 326 (1.7), 325 (0.4), 121 (16.2), 120 (10.1), and 119 (100). Anal. Calcd for $C_{25}H_{32}O_3S_2$: C, 67.53; H, 7.25. Found: C, 67.21; H, 7.30.

8: 0.069 g (24%); IR 1730 (ester) and 1700 cm^{-1} (ketone); ^1H NMR δ 7.64 and 7.61 (each s, 2 H, H-11 and H-14), 3.85 (dd, J = 7.6 and 2.7 Hz, 1 H, H-17), 3.67 and 3.65 (each s, 1.5 H, CO_2CH_3 of *R*,*S* epimers), 3.52–3.20 (m, 4 H, 2 × CH_2S), 3.11–2.96 (m, 2 H, H-7α,β), 2.88 (dd, J = 19.1 and 7.6 Hz, H-16), 2.66 (dd, J = 19.1 and 2.7 Hz, H-16), 1.59 and 1.54 (each s, 1.5 H, CH_3CS_2 of *R*,*S* epimers), 1.27 and 1.19 (each s, 3 H, 2 × CH_3); ^{13}C NMR δ 205.03 (C), 178.84 (C), 151.20 (C), 150.67 (C), 143.00 (C), 136.16 (C), 127.77 (CH), 119.37 and 119.10 (CH), 70.43 (C), 51.98 (CH_3), 50.48 (CH), 47.45 (C), 44.38 (CH), 44.16 (CH_2), 40.23 (CH_2), 39.73 (CH_2), 37.90 (CH_2), 37.45 (C), 36.61 (CH_2), 30.79 and 30.72 (CH_2), 29.68 and 29.44 (CH_3), 25.02 (CH_3), 21.25 (CH_2), 18.36 (CH_2), 16.50

(CH_3); MS, m/e 444 (0.2, M^+), 385 (0.4), 326 (1.2), 325 (0.4), 121 (26.3), 120 (15.9) and 119 (100). Anal. Calcd for $C_{25}H_{32}O_3S_2$: C, 67.53; H, 7.25. Found: C, 66.98; H, 7.32.

4α-Carbomethoxy-4β-methyl-18-nor-5α-pregna-8,11,13-triene-15,20-dione (9). (a) From Pure 7. To a solution of **7** (0.101 g, 0.227 mmol) in 4.8 mL of MeOH and 1.2 mL of THF was added a solution of $Tl(NO_3)_3 \cdot 3H_2O$ (0.252 g, 0.567 mmol, 2.5 equiv) in 1.2 mL of MeOH. The resulting solution was stirred at room temperature for 15 min, the white crystalline precipitate was filtered off and the filtrate was evaporated to leave a solid residue, which was extracted with chloroform. The extract was washed with water and dried over Na_2SO_4. Evaporation of the dried solution gave a solid, which was purified by flash chromatography with hexane–ethyl acetate (8:2) as eluent to give the diketone **9** (0.067 g, 80%) as a solid: mp 182–186 °C (from methanol); IR 1720 (ester), 1710 and 1695 (ketone), 1575 and 1600 cm^{-1} (Ar ring); ^1H NMR, δ 7.48 (d, J = 8.5 Hz, 1 H, H-12), 7.26 (d, J = 8.5 Hz, 1 H, H-11), 4.20 (br t, J 5.7 Hz, 1 H, H-17), 3.63 (s, 3 H, CO_2CH_3), 3.40 (dd, J = 6.7 and 19.5 Hz, 1 H, H-7β), 3.15–2.90 (m, 1 H, H-7α), 2.81 (deformed d, J = 6.0 Hz, 2 H, H-16α,β), 2.22 and 2.17 (each s, 3 H, CH_3CO of *R,S* epimers at C-17), 1.25 and 1.19 (each s, 3 H, 2 × CH_3) [irradiation at δ 4.20 collapsed the signal at δ 2.81 to a singlet and irradiation at δ 1.65 collapsed the doublet of doublets at δ 3.40 to a doublet (J = 19.2 Hz) and the multiplet at δ 3.15–2.90 to a deformed doublet (J = 19.3 Hz)]; ^{13}C NMR δ 206.21 (C), 204.87 (C), 178.69 (C), 150.56 and 150.44 (C), 149.96 and 149.91 (C), 137.16 (C), 133.90 (C), 131.17 and 131.11 (CH), 123.36 (CH), 51.96 (CH_3), 51.12 and 50.98 (CH), 47.45 (C), 44.23 and 44.04 (CH), 40.08 (CH_2), 38.26 and 38.12 (CH_2), 37.44 (C), 36.34 (CH_2), 28.01 and 27.62 (CH_3), 26.95 and 26.78 (CH_2), 25.00 (CH_3), 20.73 (CH_2), 18.42 (CH_2) and 16.39 (CH_3); MS, m/e (relative intensity) 369 (M^+ + 1, 19.4), 368 (M^+, 72.5), 326 (26.5), 325 (19.8), 293 (62.5), 265 (32.0), and 43 (100); HRMS, calcd for $C_{23}H_{28}O_4$ 368.1987, found 368.1991. Anal. Calcd: C, 74.97; H, 7.66. Found: C, 74.62; H, 7.46.

(b) From the Crude Cyclization Reaction Mixture. The crude reaction mixture obtained from cyclization reaction of **6** (0.150 g) was treated with $Tl(NO_3)_3 \cdot 3H_2O$ as described for pure **7**. Purification by flash chromatography with hexane–ethyl acetate (8:2) as eluent gave **9** (0.046 g, 38.5% from **5b**) and **10** (0.025 g, 21% from **5b**). **10**: IR 1690–1740 (strong br band of ester and ketone), 1610 and 1575 cm^{-1} (Ar ring); ^1H NMR δ 7.68 (s, 1 H, H-11), 7.18 (s, 1 H, H-14), 4.22 (m, 1 H, H-17), 3.65 (s, 3 H, CO_2CH_3), 2.98 (m, 2 H, H-7α,β), 2.85 (m, 2 H, H-16α,β), 2.22 and 2.18 (each s, 1.5 H, $COCH_3$ of *R,S* isomers at C-17), 1.26 and 1.17 (each s, 3 H, 2 × CH_3); ^{13}C NMR δ 206.00 (C), 203.95 (C), 178.74 (C), 151.13 and 151.03 (C), 148.15 (C), 144.21 and 144.15 (C), 134.51 (C), 126.54 (CH), 120.19 and 120.13 (CH), 51.99 (CH_3), 51.51 and 51.37 (CH), 47.40 (C), 44.42 and 44.22 (CH), 39.60 (CH_2), 38.01 and 37.91 (CH_2), 37.52 (C), 36.55 (CH_2), 30.62 and 30.54 (CH_2), 28.06 and 27.71 (CH_3), 25.00 (CH_3), 21.10 (CH_2), 18.32 (CH_2), and 16.48 (CH_3); MS, m/e (relative intensity) 369 (M^+ + 1, 7.7), 368 (M^+, 31.1), 341 (15.6), 340 (9.8), 341 (15.6), 326 (54.3), 293 (33.4), 265 (24.2), and 43 (100); HRMS, calcd for $C_{23}H_{28}O_4$ 368.1987, found 368.1982.

4α-Carbomethoxy-4β-methyl-18-nor-5α-pregna-8,11,13-trien-20-one (13). A mixture of diketone **9** (0.065 g, 0.176 mmol) and 10% Pd–C (0.065 g) in AcOH (5 mL) was shaken at room temperature under and H_2 atmosphere overnight. After removal of the catalyst by filtration through a pad of silica gel the filtrate was concentrated in vacuo. The residual oil was dissolved in acetone (6 mL) and was treated at 0 °C with a few drops of the Jones reagent. The mixture was poured into water and was extracted with ether. The organic phase was washed with 5% $NaHCO_3$ solution, dried (Na_2SO_4), and evaporated. The oily residue was purified by flash chromatography (hexane–ether, 1:1, as eluent) to give an epimeric mixture of **13a** and **13b** (0.050 g, 80%) as an oil. Both isomers (30 mg of above mixture) were separated by preparative HPLC on a μ-Porasil column in 6–8-mg portions, with hexane–ethyl acetate (95:5) as eluent, to give pure 17αH-isomer **13a** (14 mg) and 17βH-isomer **13b** (13 mg).

13a: mp 129–131°C (from hexane); $[\alpha]^{24}_D$ +5.7° (c 0.24, $CHCl_3$); IR 1717 (ester) and 1707 cm^{-1} (ketone); ^1H NMR δ 7.08 (AB q, J = 8.2 Hz, 2 H, H-12 and H-11), 4.04 (dd, J = 5.9 and 7.9 Hz, 1 H, H-17α), 3.64 (s, 3 H, CO_2CH_3), 2.97–2.60 (m, 4 H, H-15α,β and H-7α,β), 2.40–2.20 (m, 4 H, H-16α,β, H-5α, and H-1β), 2.17 (s, 3 H, $COCH_3$), 1.26 (s, 3 H, 4-CH_3), 1.19 (s, 3 H, 10-CH_3) [the signal at δ 4.04 collapsed to a singlet when irradiated at δ 2.31]; ^{13}C NMR δ 209.17 (C), 179.07 (C), 148.83 (C), 143.14 (C), 137.44 (C), 131.64 (C), 122.90 (CH), 121.95 (CH), 58.77 (CH), 51.89 (CH_3), 47.63 (C), 44.53 (CH), 38.30 (CH_2), 37.14 (C), 36.60 (CH_2), 30.44 (CH_2), 28.04 (CH_2), 27.80 (CH_2), 27.80 (CH_3), 25.10 (CH_3), 21.36 (CH_2), 18.55 (CH_2), and 16.46 (CH_3).

13b: mp 143–145 °C (from hexane); $[\alpha]^{24}_D$ +73.7° (c 0.24, $CHCl_3$); IR 1721 (ester) and 1700 cm^{-1} (ketone); ^1H NMR δ 7.07 (AB q, J = 8.2 Hz, 2 H, H-12 and H-11), 4.05 (t, J = 7 Hz, H-17β), 3.65 (s, 3 H, CO_2CH_3), 2.90–2.63 (m, 4 H, H-15α,β and H-7α,β), 2.38–2.17 (m, 4 H, H-16α,β, H-5α, and H-1β), 2.14 (s, 3 H, $COCH_3$), 1.26 (s, 3 H, 4-CH_3), 1.19 (s, 3 H, 10-CH_3); ^{13}C NMR δ 209.17 (C), 179.06 (C), 148.93 (C), 143.16 (C), 137.52 (C), 131.68 (C), 122.99 (CH), 121.97 (CH), 58.93 (CH), 51.92 (CH_3), 47.65 (C), 44.43 (CH), 38.17 (CH_2), 37.14 (C), 36.59 (CH_2), 30.48 (CH_2), 28.11 (CH_2), 27.74 (CH_2), 27.58 (CH_3), 25.22 (CH_3), 21.36 (CH_2), 18.56 (CH_2), and 16.48 (CH_3).

Both isomers showed MS, m/e (relative intensity) 355 (M^+ + 1, 0.5), 354 (M^+, 1.8), 326 (1.2), 311 (22.3), 285 (10.9), and 43 (100); HRMS, calcd for $C_{23}H_{30}O_3$ 354.2195, found 354.2201.

Preparation of Methyl Abieta-8,11,13,15-tetraen-18-oate (2) from the Oxidation–Pyrolysis Products of Methyl Dehydroabietate (1b). A mixture of methyl 13-acyl-7-oxopodocarpa-8,11,13-trien-18-oate and methyl 7-oxoabieta-8,11,13,15-tetraen-18-oate was prepared from methyl dehydroabietate **1b** by the modified procedure of Sanderson.[4b] The mixture was purified by flash chromatography with hexane–ethyl acetate (1:1) as eluent to give methyl 7-oxoabieta-8,11,13,15-tetraen-18-oate (30% from **1b**): mp 83–85 °C (from hexane–ethyl acetate) (lit.[4b] mp 83–84 °C).

A solution of the above ketone (0.212 g, 0.65 mmol), potassium hydroxide (0.44 g, 7.84 mmol), and 80% hydrazine hydrate (0.36 mL, 7.40 mmol) in diethylene glycol (4.9 mL) was heated at 110 °C for 2 h and then at 210 °C for 2 h. After addition of more potassium hydroxide (0.3 g) the solution was heated for 1 h at the same temperature. The cooled reaction mixture was poured into cold water, acidified with dilute hydrochloric acid, and extracted with ether. The organic layer was washed with brine followed by drying and removal of the solvent to afford a yellowish oil, which was esterified with diazomethane. Chromatography (hexane–ether 9:1) gave methyl abieta-8,11,13,15-tetraen-18-oate (**2**) (0.185 g, 91%) as a solid: mp 74–75 °C (from methanol); $[\alpha]^{25}_D$ +64 (c 0.28, $CHCl_3$); IR 1725 (ester), 1630 (olefine) and 1500 cm^{-1} (Ar ring); ^1H NMR δ 7.23–7.12 (m, 3 H, Ar protons), 5.30 and 5.01 (each br s, 1 H, 2 × CH=), 3.66 (s, 3 H, CO_2CH_3), 2.93–2.85 (m, 2 H, H7α,β), 2.11 (s, 3 H, $=CCH_3$), 1.27 and 1.20 (each s, 3 H, 2 × CH_3); ^{13}C NMR δ 178.90 (C), 148.73 (C), 142.89 (C), 138.20 (C), 134.62 (C), 125.99 (CH), 124.02 (CH), 122.95 (CH), 111.52 (CH_2), 51.81 (CH_3), 47.54 (C), 44.74 (CH), 37.85 (CH_2), 37.00 (C), 36.56 (CH_2), 29.96 (CH_2), 24.89 (CH_3) , 21.68 (CH_3), 21.59 (CH_2), 18.47 (CH_2), and 16.44 (CH_3).

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Registry No. **1a**, 1740-19-8; **1b**, 1235-74-1; **2**, 22465-60-7; **3**, 53655-52-0; **4a** (isomer 1), 114958-33-7; **4a** (isomer 2), 114958-34-8; **5** (isomer 1), 114958-35-9; **5** (isomer 2), 114958-36-0; **6** (isomer 1), 114958-37-1; **6** (isomer 2), 114958-38-2; **7** (isomer 1), 114978-20-0; **7** (isomer 2), 115015-36-6; **8** (isomer 1), 114958-39-3; **8** (isomer 2), 115015-37-7; **9** (isomer 1), 114958-40-6; **9** (isomer 2), 115015-38-8; **11** (isomer 1), 114958-41-7; **11** (isomer 2), 115015-39-9; **12** (isomer 1), 114958-42-8; **12** (isomer 2), 115015-40-2; **13a**, 114958-43-9; **13b**, 115015-41-3; DDQ, 84-58-2; 4α-carbomethoxy-20-hydroxy-4β-methyl-18-nor-5α-pregna-8,11,13-triene, 114958-44-0; 4α-carbomethoxy-20-hydroxy-4β-methyl-18-nor-5α,17α-pregna-8,11,13-triene, 115015-42-4; methyl 7-oxoabieta-8,11,13,15-tetraen-18-oate, 17751-36-9.