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NEW SERRATANE TRITERPENES FROM WESTERN WHITE PINE BARK

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Abstract - Three new serratanes were isolated from the nonsaponifiable fraction of western white pine (Pinus monticola Dougl.) bark. The compounds were shown to be 3β-methoxyserrat-14-ene-21α,30-diol (8a), 3β-methoxyserrat-14-ene-21α,29-diol (9a), and 3β-methoxyserrat-14-ene-21β,30-diol (10a), by a combination of chemical, and spectral methods.

Key Words: Serratane, triterpenes, western white pine, bark, Pinus monticola, ^{1}H-NMR, ^{13}C-NMR, mass spectra.

INTRODUCTION

Terpenoids, waxes, fats, steroids, fatty (and wax) acids, wax alcohols, and resins contained in wood and bark are extracted by nonpolar organic solvents. Marketable components of this nature are now recovered as byproducts of wood pulping (i.e., tall oil and related naval stores[1]) and as waxes.[2] Detailed knowledge of the chemistry of bark extractives is needed to assess the potential for using the waste bark from lumber and pulp production as a source of chemicals, and to determine the types of components that might interfere with the pulping process due to bark remaining on the pulping chips.

Western white pine (Pinus monticola Dougl.) is a major lumber species in the northwestern United States and southwestern Canada. A preliminary investigation of the chemistry of western white pine bark[3] showed that it contained a significant amount of benzene-extractable constituents. In a detailed study of the benzene extract conducted to determine its overall chemical composition,[4] the extract was separated into acidics and neutrals. The acidics contained fatty, wax, and resin acids. The neutrals were further fractionated into free sterols, esterified sterols and other esters, waxes, wax alcohols, and nonsaponifiables.

The nonsaponifiables were separated into more than 70 individual compounds.[4] This included a number of triterpenes that were interrelated in that they contained a lanostane skeleton.[5] A second group of triterpenes with a serratane skeleton was also isolated and their structures determined by comparison with authentic serratanes.[4] A third group of triterpenes were isolated from the nonsaponifiables (compounds A-H).[4] Preliminary data suggested this last group of triterpenes were previously unreported serratane derivatives.

Serratanes are a novel group of naturally occurring pentacyclic triterpenes in which the central C-ring is seven-membered. Serratane triterpenes have been found in such diverse plants as conifers (especially Pinus and Picea species),[6,7] club mosses (Lycopodium species),[6,7] a

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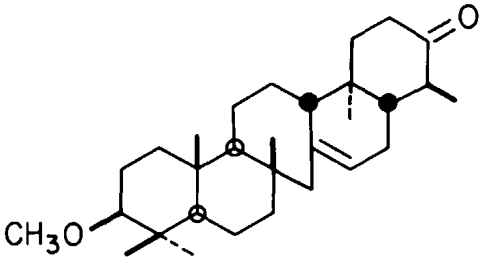

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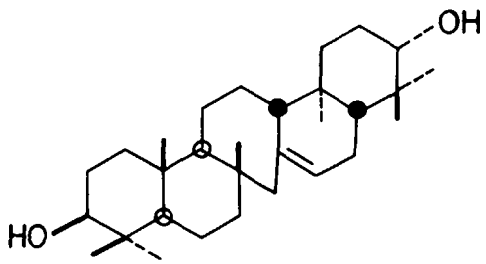

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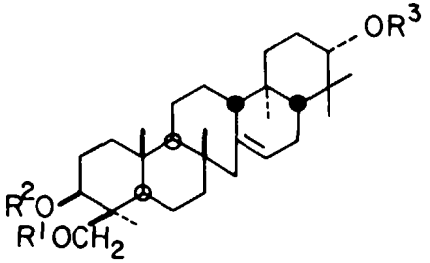

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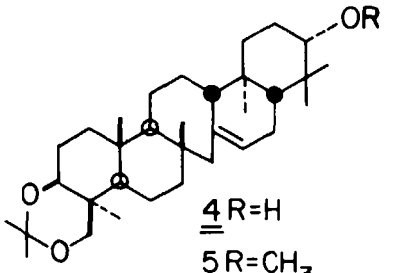

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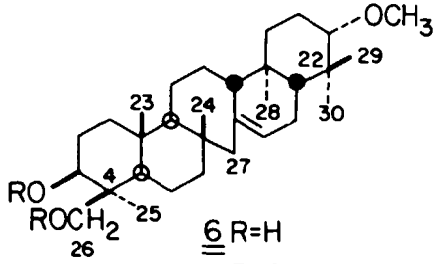

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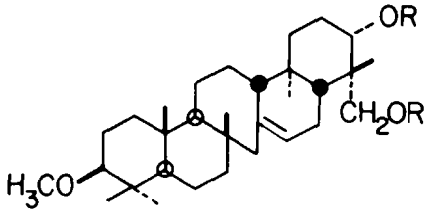

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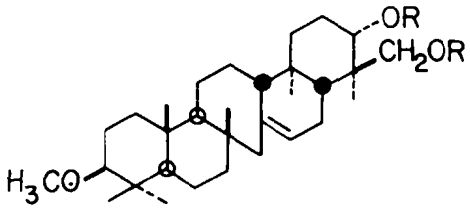

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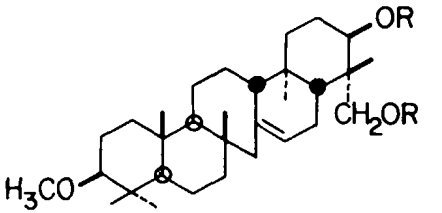

10a R=H

10b R=Ac

fern,[8] and more recently Homogyne alpina,[9] and the liverwort, Nardia scalaris.[10] All known examples of serratane triterpenes have seven tertiary methyls (one or more of which may occur as a hydroxymethyl) and usually have oxygen functionalities at C(3) and C(21).

We reported[11] that the structure of one of the unknown serratane triterpenes (compound H) from western white pine bark was 3β-methoxy-30-norserrat-14-en-21-one (1). We now wish to report the structural elucidation of three related serratane triterpenes, compounds A, B, and C. Compounds F and G were isolated in insufficient quantity to allow further characterization. Compound D was a mixture of components, the major component probably being an autoxidation product formed from a serratane derivative within the bark. Compound E is not a serratane.

RESULTS AND DISCUSSION

Triterpenes A, B, and C.

Triterpenes A, B, and C are extremely polar--i.e., they are retained on column chromatography and TLC--and must be eluted with solvents more polar than those used to remove serratenediol (2). Their polar nature also renders them very insoluble in common organic solvents. Due to their poor solubility, the ^{1}H-NMR spectra of A, B, and C were not completely satisfactory. However, the ^{1}H-NMR data did reveal that all three triterpene alcohols had the following features in common: (1) six tertiary methyls, (2) an equatorial secondary methoxyl group, (3) a tertiary hydroxymethyl group, (4) a secondary hydroxyl group, and (5) a vinyl hydrogen. These data suggested the compounds were serratanes having three oxygen functionalities.

Rogers[12] has isolated an unknown serratriol monomethyl ether from Sitka spruce. A sample of this compound, which had the same solubility properties, was identical to compound A by TLC comparison. Comparison by IR was not completely satisfactory, apparently due to different impurities in both samples.

To overcome the solubility problems and to afford a means of purification, triterpenes A, B, and C were acetylated and purified by column chromatography. High resolution mass spectra established that all three acetates had an empirical formula of $C_{35}H_{56}O_5$ indicating a serratane skeleton having a methoxyl and two acetoxyl moieties.

The ^{1}H-NMR data for the three diacetates are summarized in Table I. The NMR data resemble those obtained from synthetic serratriol triacetate (3b) indicating that these compounds are monomethoxyl, diacetoxyl derivatives of a serratriol isomer.

Structure of Triterpene A Diacetate (8b).

The data in Table I show that the signals in the ^{1}H-NMR spectrum of triterpene A diacetate attributed to the six methyls and two acetate moieties are comparable with corresponding groups in serratriol triacetate. The quartet at δ 2.62 can be assigned to an axial hydrogen geminal to the methoxyl group, which must, therefore, be secondary and equatorial. As in the spectrum of serratriol triacetate, the AB dd centered at δ 4.31 indicates the axial nature of the acetoxymethyl group.[13-24] Further, the triplet at δ 4.59 is assignable to an axial hydrogen geminal to a secondary acetoxyl group. Therefore, the secondary acetoxyl group is equatorial as are the secondary acetoxyl groups in serratriol triacetate. The ^{1}H-NMR spectrum of A diacetate is superimposable over that of the diacetate obtained from Rogers' serratriol monomethyl ether from Sitka spruce.

Structure 7, which fits this data, was eliminated by comparison of A diacetate with a sample of compound 7 synthesized from serratriol (3a) by the following method. Serratriol (3a) was converted to its acetonide (4), which was methylated with methyl iodide to give serratriol acetonide 21-methyl ether (5). This was converted to serratriol 21-methyl ether (6), which on acetylation gave the desired compound 7. TLC and NMR comparison of synthetic compound 7 with compound A diacetate showed that the two compounds were not the same. The spectral data, however, indicated that the compounds are extremely similar and thus are probably isomeric.

Table I.--^{1}H-NMR spectral data for A diacetate, B diacetate, and C diacetate compared with those for serratriol triacetate and serratriol 21-methyl ether diacetate

Compound	Chemical shift (δ) and multiplicity						
	C-C<u>H</u>$_3$	OAc	C<u>H</u>OCH$_3$	OC<u>H</u>$_3$	C<u>H</u>$_2$OAc	C<u>H</u>OAc	C=C<u>H</u>
A diacetate (<u>8b</u>)[a]	0.70,0.75 0.80,0.82 0.95,0.98 (all s)	2.04 (s) 2.05 (s)	2.62 (q,J=4,11.8 Hz)	3.35 (s)	4.31 (AB dd, δ_A=4.17, δ_B=4.46, J=11.8 Hz)	4.59 (t,J=8 Hz)	5.31 (br s)
B diacetate (<u>9b</u>)[a]	0.72,0.75 0.81,0.84 0.89,0.95 (all s)	2.02 (s) 2.06 (s)	2.62 (q,J=3.7,11.8 Hz)	3.35 (s)	3.75 (AB dd, δ_A=3.67 δ_B=3.82 J=11.4 Hz)	4.79 (q,J=4.4,11.4 Hz)	5.31 (br s)
C diacetate (<u>10b</u>)[a]	0.70,0.75 0.82,0.86 0.95,0.96 (all s)	2.07 (s) 2.10 (s)	2.63 (q,J=4,11.8 Hz)	3.35 (s)	4.16 (AB dd, δ_A=4.10, δ_B=4.22, J=11.4 Hz)	5.01 (br s)	5.32 (br s)
Serratriol triacetate (<u>3b</u>)[b]	0.70,0.85 0.85,0.85 0.90,1.00 (all s)	2.03 2.05 2.05 (all s)	--	--	4.24 (AB dd, δ_A=4.12, δ_B=4.36, J=11.5 Hz)	4.55 (br m)	5.35 (m)
Serratriol 21-methyl ether diacetate (<u>4</u>)[b]	0.67,0.83 0.83,0.83 0.93,0.98 (all s)	2.03 (s) 2.08 (s)	2.65 (q,J=3,9 Hz)	3.36 (s)	4.25 (AB dd, δ_A=4.12, δ_B=4.38, J=11.5 Hz)	4.57 (br m)	5.33 (m)

[a] 270 MHz.
[b] 60 MHz.

The compelling feature of structure 7 was that the chemical shifts expected for the C(3)-H and C(26)-H in that structure were compatible with the chemical shifts observed in the ^{1}H-NMR spectrum of A diacetate. The only other structure that accommodates this relationship is one in which the acetoxyl and acetoxymethyl moieties are at C(21) and C(30), respectively, and the methoxyl moiety is at C(3). This leads to the conclusion that structure 8b is the correct structure of triterpene A diacetate and 8a the structure of triterpene A and of Rogers' Sitka spruce triterpene.

The chemical shifts of the tertiary methyls in the 270 MHz ^{1}H-NMR of compound A diacetate support this structure as revealed by comparison with the ^{1}H-NMR of similar compounds.[14,19,24-28] In addition, the relative stereochemistry at C(21) and C(22) of structure 8b is consistent with the chemical shifts assigned to the C(21)-H and the C(30)-H_2 in structure (8b).[13-24]

That 8b is the correct structure for compound A diacetate is further substantiated by comparison of the mass spectrum with mass spectra reported for other serratanes,[25] and by comparison of the ^{13}C-NMR spectrum (Table II) with ^{13}C-NMR spectra of compounds having similar substructures.[26-30]

Triterpene B Diacetate (9b).

The spectral data (Tables I and II) indicate that the structure of triterpene B diacetate is similar to that of triterpene A diacetate. Comparison of the chemical shifts of the tertiary methyls show that A diacetate and B diacetate differ in configuration at C(22). This configurational difference is further substantiated by the AB dd at δ 3.75 and the quartet at δ 4.79 in the ^{1}H-NMR spectrum of B diacetate and the singlet at δ 3.48 ($-CH_2-O$) in the ^{1}H-NMR spectrum of B acetonide (11).[13-24] Further evidence of the structural similarity of A diacetate and B diacetate is provided by the mass spectral data. Except for variations in intensities, the mass spectrum of triterpene B diacetate is identical with that of triterpene A diacetate. Thus, compound B diacetate can be represented by structure 9b. The conversion of triterpenes B to compound 1, described below, adds further support for this structural assignment.

Triterpene C Diacetate (10b).

The spectral data (Tables I and II) also indicate that triterpene C diacetate is isomeric with triterpene A diacetate. The chemical shifts of the tertiary methyls are consistent with A diacetate and C diacetate differing in configuration at C(21). This configurational difference is supported by the AB dd at δ 4.16 and the 1H singlet at δ 5.01 in the ^{1}H-NMR spectrum of C diacetate.[13-24] Except for variations in intensities, the mass spectrum of triterpene C diacetate is identical to that of triterpenes A diacetate and B diacetate providing further evidence for the structural similarity of C diacetate with these compounds. Therefore, compound C diacetate can be represented by structure 10b.

Thus the structures of these new natural products were shown to be 3β-methoxyserrat-14-ene-21α,30-diol (8a), 3β-methoxyserrat-14-ene-21α,29-diol (9a), and 3β-methoxyserrat-14-ene-21β,30-diol (10a). Related serratenetriol derivatives have been isolated as natural products.[13,31,32]

Conversion of Triterpene B to Compound 1.

Triterpene B was converted to compound 1 by the following scheme.

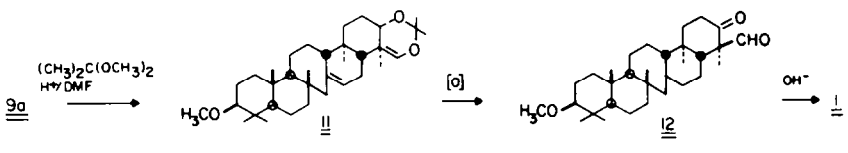

Figure 1.--Interconversion of triterpenes B (9a) and compound 1.

Table II.--^{13}C-NMR spectra of serratane triterpenes from western white pine bark

Carbon	Compound			
	A diacetate[a]	B diacetate[b]	C diacetate[b]	Compound H[b]
	δ (ppm)			
1	38.6	38.8	38.6	38.9
2	22.5	22.3	22.7	22.4
3	88.6	88.3	88.4	88.4
4	38.3	38.4	38.9	38.5
5	56.1	55.9	56.3	56.4
6	18.9	18.7	18.8	18.8
7	37.0	37.0	37.2	37.1
8	41.1	40.5	40.3	38.9
9	57.1	57.3	57.4	57.4
10	35.9	36.2	35.7	36.1
11	24.5	23.5	23.7	25.7
12	27.3	26.9	27.2	27.3
13	63.0	62.8	63.0	62.8
14	138.3	138.2	138.5	138.6
15	121.8	121.2	121.6	121.6
16	25.6	25.2	25.5	29.5
17	50.6	42.6	45.3	45.7
18	56.4	56.1	56.3	56.1
19	37.2	38.1	38.3	38.3
20	21.8	23.5	21.5	37.9
21	80.3	74.3	73.3	212.9
22	39.0	35.7	31.7	49.4
23	15.8	15.6	15.7	15.7
24	19.9	19.7	19.9	19.8
25	28.2	28.0	28.2	28.2
26	16.2	16.1	16.2	16.2
27	45.3	45.1	45.3	45.2
28	13.8	13.9	14.0	11.5
29	24.3	64.9	22.4	11.0
30	64.0	12.1	66.2	--
$O\underline{C}H_3$	57.7	56.6	56.9	54.5
$O-\overset{O}{\overset{\|}{\underline{C}}}-CH_3$	21.1 21.2	20.8 21.0	20.9 21.2	-- --
$C-\overset{O}{\overset{\|}{\underline{C}}}-CH_3$	170.5 170.8	170.2 170.7	170.4 171.0	-- --

[a] $CDCl_3$, 22.6 MHz.
[b] $CDCl_3$, 15 MHz.

Thus, triterpene B (9a) was converted to the acetonide (11). The ^{1}H-NMR of triterpene B acetonide (11), especially the singlet at δ 3.48 (C(29)-$\underline{H}_2$) and the quartet at δ~3.5 (C(21)-$\underline{H}$), are consistent[13-24] with the conformation of the 21α,29-diol grouping in the proposed structure of triterpene B. The acetonide was converted via the intermediate keto-aldehyde (12) to 3β-methoxy-30-norserrat-14-en-21-one (1); identity with the natural product[11] (compound 1) was established by GLC, TLC, IR, and NMR comparison.

This series of reactions clearly interrelates triterpenes B and compound 1. Since the structure of compound 1 was confirmed by x-ray crystallographic methods,[11,33] this interrelation establishes the full skeletal stereochemistry of triterpene B and thus by inference the stereochemistry of triterpenes A and C, which were shown to differ from B only in their orientation about the 1,3-diol moiety.

Compound 1 was the first reported naturally occurring norserratane. However, this compound may not be a true natural product since it might have true been formed from triterpene A, B, or C via the C(22)-aldehyde. Indeed, traces of serratane aldehydes were indicated in some mixtures, but they were too labile to isolate.

EXPERIMENTAL

Melting points were determined in evacuated, sealed capillaries and were corrected. Optical rotations were determined in $CHCl_3$(c 1.0). NMR spectra were measured in $CDCl_3$ and are reported in ppm relative to TMS (δ=0).

Fractionation of Benzene Extract.

Fractionation of the benzene extract of western white pine bark and isolation of compounds A, B, and C was previously described.[4]

Compound A diacetate (8b). Impure compound A was acetylated with pyridine and acetic anhydride at room temperature for 36 h. The reaction was stopped by the addition of methanol. The reaction product was isolated by evaporation (in vacuo) of the pyridine-methyl acetate and purified by column chromatography on silica gel. Benzene-ether (98:2) eluted compound A diacetate (8b): mp 237-239 °C. A diacetate was filtered through alumina (Act. III, neutral) with CH_2Cl_2. A small yellow band was retained by the alumina. Crystallization of A diacetate from hexane gave a material with mp 260-260.5 °C; $[\alpha]_D^{24}$ + 6.5° (c 0.3). ν_{max}^{KBr}, cm^{-1}: 1735, 1245 (OAc). ^{1}H-NMR (270 MHz): Table I. ^{13}C-NMR (22.63 MHz): Table II. MS (probe,70 eV), m/z (rel. int.): 556(1; M^+), 497(17), 496(52; $C_{33}H_{52}O_3$), 482(12), 481(38), 437(20), 436(58; $C_{31}H_{48}O$), 423(20), 422(26), 421(81; $C_{30}H_{45}O$), 404(17), 389(20; $C_{29}H_{41}$), 361(43; $C_{23}H_{37}O_3$), 356(20; $C_{25}H_{40}O$), 323(8), 324(5), 316(1), 284(4), 267(32; $C_{20}H_{27}$), 255(17), 253(20), 251(17), 241(17), 239(17), 237(12), 235(15; $C_{16}H_{27}O$), 234(12; $C_{16}H_{26}O$), 227(26; $C_{17}H_{23}$), 225(23; $C_{17}H_{21}$), 221(41; $C_{15}H_{25}O$), 217(20; $C_{16}H_{25}$), 215(17), 213(26), 211(23), 209(15), 203(41; $C_{15}H_{23}$). 202(32; $C_{15}H_{22}$), 201(46; $C_{15}H_{21}$), 200(35; $C_{15}H_{20}$), 199(49; $C_{15}H_{19}$), 198(17), 197(35; $C_{15}H_{17}$), 191(19), 190(26), 189(72; $C_{14}H_{21}$), 188(26), 187(70; $C_{14}H_{19}$), 186(26), 185(64; $C_{14}H_{17}$), 184(20), 183(49), 180(4), 181(15), 177(22; $C_{13}H_{21}$), 176(12), 175(38; $C_{13}H_{19}$), 174(20), 173(46; $C_{13}H_{17}$), 172(16), 171(41; $C_{13}H_{15}$), 170(16), 169(29; $C_{13}H_{13}$), 167(12), 163(26), 162(20), 161(70), 160(26), 159(58; $C_{12}H_{15}$), 158(17), 157(42), 156(16), 155(23), 149(35), 148(23), 147(67), 146(26), 145(72), 144(20), 143(35), 142(17), 141(15), 137(29), 136(29), 135(72; $C_{10}H_{15}$), 134(35), 133(75), 132(20), 131(46), 123(36), 122(20), 121(100; C_9H_{13}), 120(41), 119(84; C_9H_{11}), 117(23), 109(51), 107(88), 105(75; C_8H_9).

Serratriol acetonide (4). Serratriol (3a) (400 ml) was dissolved in dimethylformamide (8 ml) and 2,2-dimethoxy propane (4 ml) to which was added p-toluenesulphonic acid (35 mg), and the mixture refluxed for 2 h. The reaction mixture was cooled, neutralized with solid $NaHCO_3$ (400 mg), filtered, evaporated in vacuo to dryness, dissolved in benzene, and chromatographed over alumina. Elution with benzene afforded a deep yellow-colored semisolid (620 mg) that was crystallized three times: mp 225-228 °C and 310-315 °C (dimorphic). Reported:[34] mp 250-252 °C. ν_{max}^{KBr}, cm^{-1}: 3490 (OH); 1630, 800 (C=CH); 1103 (C-O-C). ^{1}H-NMR (60 MHz): δ 0.66, 0.83, 0.96, 1.07, 1.14 (18H,6

tertiary Me); 1.40, 1.35 (6H,two s,$Me_2C<^{O}_{O}$); 3.59 (2H,AB dd[δ_A=3.19, δ_B=3.99],J=11.5 Hz,C-C$\underline{H}_2$-O); 3.48 (2H,m,C$\underline{H}$OH and C$\underline{H}$OC); 5.32 (C=C$\underline{H}$). Reported NMR: 1.40, 1.35 (6H,d,$Me_2C<^{O}_{O}$), 3.16 and 3.99 (a pair of d's,J=12 Hz,C-C$\underline{H}_2$-O-C), 3.39 (2H,m,C$\underline{H}$OH and C$\underline{H}$OC).[34]

Serratriol acetonide 21-methyl ether (5). Serratriol acetonide (200 mg) was dissolved in dry ether (25 ml) to which was added KO$\underline{t}$Bu (5 g) dissolved in dry ether (200 ml). The reaction mixture was swirled for 2 min. Then methyl iodide (7 ml) was added. The solution was swirled and left at room temperature for 72 h, with occasional shaking. The reaction mixture was poured into water and extracted with ether. The combined ether layers were washed with water, 10% sodium thiosulfate, and water, and dried over magnesium sulfate. The ether was evaporated to yield 212 mg of serratriol acetonide 21-methyl ether, which was crystallized to constant mp 133-135 °C and 147-148 °C (dimorphic), $[\alpha]_D^{25}$ + 25°. Found: C, 79.67; H, 11.10%. Calculated for $C_{34}H_{56}O_3$: C, 79.63; H, 11.01%. ν_{max}^{KBr}, cm^{-1}: 1630 (C=C), 1105 (C-O-C). ^{1}H-NMR (60 MHz): δ 0.67, 0.81, 0.84, 0.95, 1.09, 1.15 (18H,6 tertiary Me), 1.36, 1.48 (6H,two s,$Me_2C<^{O}_{O}$), 2.68 (1H,br m,C$\underline{H}$OMe axial), 3.38 (3H,s,OMe), 3.59 (2H,AB dd[δ_A=3.19, δ_B=3.99],J=11.5 Hz,C-C$\underline{H}_2$-O), 5.33 (C=C$\underline{H}$).

Serratriol 21-methyl ether (6). Serratriol acetonide 21-methyl ether (190 mg) was hydrolyzed in two batches by refluxing with p-toluenesulfonic acid (130 mg) in $CHCl_3$-ethanol (95:5) (25 ml) for 2 h. The product was cooled, diluted with $CHCl_3$ (200 ml), washed with 1N NaOH and H_2O, and dried over $MgSO_4$. Removal of the solvent afforded 180 mg of serratriol 21-methyl ether that was crystallized to constant mp 342-344 °C, $[\alpha]_D^{25}$ + 2° (c 0.7). Found: C, 78.79; H, 11.25%. Calculated for $C_{31}H_{52}O_3$: C, 78.76; H, 11.19%. ν_{max}^{KBr}, cm^{-1}: 1630, 800 (C=CH); 1105 (C-O-C). ^{1}H-NMR (60 MHz): δ 0.66, 0.77, 0.81, 0.95, 1.21 (18H,6 tertiary Me), ~2.7 (1H,br m,C$\underline{H}$OMe axial), 3.76 (2H,AB dd[δ_A=3.34, δ_B=4.18],J=11 Hz,-C$\underline{H}_2$OH), 3.39 (3H,s,OMe equatorial) 5.36 (1H,br m,C=C$\underline{H}$).

Serratriol 21-methyl ether diacetate (7). Serratriol 21-methyl ether (120 mg) was acetylated with acetic anhydride and pyridine in the usual manner, and the resulting acetate (125 mg) was crystallized to constant mp 231-233 °C, $[\alpha]_D^{19}$ + 13°. Found: C, 75.59; H, 10.16%. Calculated for $C_{35}H_{56}O_5$: C, 75.49; H, 10.14%. ν_{max}^{KBR}, cm^{-1}: 1744 (C=O); 1630, 800 (C=CH); 1250, 1235 (C-O); 1105 (C-O-C). ^{1}H-NMR (60 MHz): Table I. TLC comparison with A diacetate showed they had different R_f's.

Compound B diacetate (9b). Impure compound B was acetylated with pyridine and acetic anhydride at room temperature for 36 h and the reaction product isolated by the methods used for A diacetate. B diacetate was crystallized from benzene-hexane: mp 237-239 °C, $[\alpha]_D^{24}$ + 44°. Found: C, 75.13; H, 10.20%. Calculated for $C_{35}H_{56}O_5$: C, 75.49; H, 10.14%. ν_{max}^{KBr}, cm^{-1}: 1745, 1245 (OAc); 1635, 790 (C=CH). ^{1}H-NMR (270 MHz): Table I. ^{13}C-NMR (15 MHz): Table II. MS (probe, 70 eV), m/z (rel. int.): 556(2; M^+, $C_{35}H_{56}O_5$), 498(16), 497(87), 496(100; M^+-HOAc, $C_{33}H_{52}O_3$), 437(56), 436(91; M^+-HOAc-HOAc, $C_{31}H_{48}O$), 423(60; $C_{30}H_{47}O$), 422(82), 421(96; $C_{30}H_{45}O$), 389(35; $C_{29}H_{41}$), 357(42), 356(89; $C_{25}H_{40}O$), 355(51; $C_{25}H_{39}O$), 354(30; $C_{25}H_{38}O$), 342(25; $C_{24}H_{38}O$), 324(18; $C_{24}H_{36}$), 323(61; $C_{24}H_{35}$), 269(23; $C_{20}H_{29}$), 268(17), 267(22), 262(47), 261(52), 260(17), 255(19), 253(33; $C_{19}H_{25}$), 241(25; $C_{18}H_{25}$), 239(19), 235(73; $C_{16}H_{27}O$), 234(73; $C_{16}H_{26}O$), 227(45), 235(37), 232(32), 221(74; $C_{15}H_{25}O$), 217(45; $C_{16}H_{25}$), 215(27; $C_{16}H_{23}$), 214(20), 213(37), 211(27), 205(22), 204(39), 203(73; $C_{15}H_{23}$), 202(74; $C_{15}H_{22}$), 201(73; $C_{15}H_{21}$), 200(64; $C_{15}H_{20}$). M^+ m/z 556.3979. Required for $C_{35}H_{56}O_5$, M^+ m/z 556.4127.

B acetonide (11). B diacetate (9b) (53 mg) was dissolved in toluene (15 ml)-methanol (50 ml). 3N NaOH (10 ml) was added and the mixture stirred under N_2 for 2 days. The mixture was partitioned between H_2O and ether in the usual manner to give white crystalline compound B (53 mg). Compound B was dissolved in DMF (30 ml); 2,2-dimethoxypropane (2 ml) and p-toluenesulfonic acid (15 mg) were added and the mixture refluxed for 2 h. After cooling, $NaHCO_3$ (400 mg) was added and the mixture filtered. The filtrate was evaporated to dryness and chromatographed over 40 g silica gel. Petroleum ether-diethyl ether (90:10) eluted 50 mg of a white crystalline solid: mp 293.5-294.5 °C, $[\alpha]_D^{24}$ - 4° (c 1.2). ^{1}H-NMR (60 MHz): δ 0.73 (3H,s,Me), 0.77 (3H,s,Me), 0.82 (3H,s,Me), 0.85 (3H,s,Me), 0.97 (3H,s,Me), 1.10 (3H,s,Me), 1.42 (6H,s,$Me_2C<^{O}_{O}$), 2.65 (1H,m,-C$\underline{H}$OMe), 3.35 (3H,s,OMe), 3.48 (2H,s,C$\underline{H}_2$-O), ~3.5 (1H,buried q?), 5.28 (1H,m,C=C$\underline{H}$).

Synthesis of 3β-methoxy-30-norserrat-14-en-21-one (1) from B acetonide (11). B acetonide (25 mg) was dissolved in acetone (20 ml)-methylene chloride (10 ml) and cooled to 0° (ice bath); a fine precipitant was observed. Kiljani reagent[35] (8 drops) was added with stirring under N_2. After 5 min the ice bath was removed and the reaction mixture stirred an additional 5 min. Methanol (5 ml) was added to stop the reaction. The mixture was isolated by partitioning between ether and successively 1N H_2SO_4, 1N NaOH, and H_2O. The combined ether layers were evaporated to give 25 mg of a white crystalline solid. ^{1}H-NMR (60 MHz): δ 9.08 (-CHO).

The material isolated above was dissolved in methanol (30 ml)-toluene (20 ml). 3N NaOH (1 ml) was added and the solution stirred under N_2 overnight. The reaction mixture was partitioned between ether and 1N H_2SO_4 and then H_2O. The ether layer was evaporated to give a light yellow solid (25 mg) that was chromatographed over 40 g silica gel. Petroleum ether-diethyl ether (90:10) eluted 5 mg B acetonide followed by 15 mg 3β-methoxy-30-norserrat-14-en-21-one (1).

The chromatographically pure material [TLC: silica gel, silica gel-$AgNO_3$; GLC:SE-30,QF-1] had mp 277-278.5°, $[\alpha]_D^{22}$ - 0.6°, ORD: $[\theta]_{286}$ + 5165 ($CHCl_3$, c 0.1). Found: C, 81.94; H, 11.26%. Calculated for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98%. ν_{max}^{KBr}, cm^{-1}: 1710 (C=O); 1630, 797 (C=CH); 1100 (C-O-C). ^{1}H-NMR (270 MHz): δ 0.75 (3H,s,Me), 0.80 (3H,s,Me), 0.83 (3H,s,Me), 0.90 (3H,s,Me), 0.96 (3H,s,Me), 0.97 (3H,d,J=7 Hz,C(22)-Me), 2.62 (1H,q,J=3 and 11 Hz,CHOMe axial), 3.35 (3H,s,OMe), and 5.34 (1H,br s,C=CH). ^{13}C-NMR (15 MHz): Table II. MS (probe, 70 eV), m/z (rel. int.): 441(38), 440(100; $C_{30}H_{48}O_2$, M^+), 425(17; $C_{29}H_{45}O_2$, M^+-Me), 409(24), 408(92; $C_{29}H_{44}O$, M^+-MeOH), 394(16; $C_{28}H_{42}O$), 393(44; $C_{28}H_{41}O$), 378.7(M*, 440→408 and 408→393) 365(38; $C_{26}H_{37}O$), 316(2), 286(5; $C_{20}H_{30}O$), 284(9), 271(33; $C_{19}H_{27}O$), 270(24; $C_{19}H_{26}O$), 269(9), 243(12; $C_{17}H_{13}O$), 229(15; $C_{16}H_{21}O$), 222(20), 221(84; $C_{15}H_{25}O$), 217(33; $C_{16}H_{25}$), 205(22), 204(85; $C_{14}H_{20}O$), 203(34; $C_{15}H_{23}$), 201(19; $C_{15}H_{21}$), 199(15; $C_{15}H_{19}$), 190(46; $C_{14}H_{22}$), 189(79; $C_{14}H_{21}/C_{14}H_{21}O$), 187(33; $C_{14}H_{19}$), 175.2(M*, 204→189), 161.8(M*, 221→189), 124(19). Found M^+ m/z 440.3674. Calculated for $C_{30}H_{48}O_2$, M^+ m/z 440.3654.

Compound C diacetate (10b). Impure compound C was acetylated with pyridine and acetic anhydride at room temperature for 60 h. The resulting diacetate was purified by chromatography over silica gel. Benzene-diethyl ether (98:2) eluted chromatographically pure compound C diacetate: mp 241-242 °C, $[\alpha]_D^{22}$ - 30°. ν_{max}^{KBr}, cm^{-1}: 1745, 1245 (OAc); 1640, 790 (C=CH). ^{1}H-NMR (270 MHz): Table I. ^{13}C-NMR (15 MHz): Table II. MS (probe, 70 eV), m/z (rel. int.): 556(1; M^+), 498(9), 496(100; M^+-HOAc, $C_{30}H_{52}O_3$), 437(28), 436(78;M^+-HOAc-HOAc, $C_{31}H_{48}O$), 423(15; $C_{30}H_{47}O$), 422(24; $C_{30}H_{46}O$), 421(80; $C_{30}H_{45}O$), 389(11; $C_{29}H_{41}$), 381(11), 357(10), 356(35; $C_{25}H_{40}O$), 355(15; $C_{25}H_{39}O$), 354(10; $C_{25}H_{38}O$), 323(14; $C_{24}H_{35}$), 269(10; $C_{20}H_{29}$), 261(13; $C_{17}H_{25}O_2$), 253(12), 235(21; $C_{16}H_{27}O$), 234(23; $C_{16}H_{26}O$), 227(20; $C_{17}H_{23}$), 221(65; $C_{15}H_{25}O$), 204(51; $C_{15}H_{24}$), 203(59; $C_{15}H_{23}$), 202(30; $C_{15}H_{22}$), 201(45; $C_{15}H_{21}$), 200(32; $C_{15}H_{20}$). M^+-HOAc m/z 496.3933. Required for $C_{56}H_{56}O_5$,M^+-HOAc m/z 496.3915.

REFERENCES

1. D. F. Zinkel, Chem. Tech. 1975, 235.
2. F. Trocino, AIChE Symp. Ser. 1975, 71, 46; In W. K. Laulner, ed., Forest Product Residuals.
3. W. C. Nickles and J. W. Rowe, Forest Prod. J. 1962, 12, 374.
4. A. H. Conner, B. A. Nagasampagi and J. W. Rowe, Phytochemistry 1980, 19, 1121.
5. J. P. Kutney, G. Eigendorf, B. R. Worth, J. W. Rowe, A. H. Conner and B. A. Nagasampagi, Helv. Chim. Acta 1981, 64, 1183.
6. M. J. Kulshreshtha, D. K. Kulshreshtha and R. P. Rastogi, Phytochemistry 1972, 11, 2369.
7. P. Pant and R. P. Rastogi, Phytochemistry 1979, 18, 1095.
8. G. Berti, F. Bottari, A. Marsilli, I. Morelli, and A. Mandelbaum, J. Chem. Soc. (Chem. Commun.) 1967, 50.
9. J. Harmatha, Czechoslovak Acad. Sci., Institute of Organic Chemistry and Biochemistry, personal communication.
10. I. Benes, T. Vanek, M. Budesinsky, and V. Herout, Phytochemistry 1981 20, 2591.
11. A. H. Conner, T. P. Harmony and M. Sundaralingam, J. Org. Chem. 1981, 46, 2987.
12. I. H. Rogers, Canadian Forest Prod. Lab., personal communication.
13. Y. Tsuda, T. Sano, A. Morimoto, M. Hatanaka and Y. Inubushi, Chem. Pharm. Bull. (Tokyo) 1974, 22, 2383.
14. A. Gaudener, J. Polonsky and E. Wenkert, Bull. Soc. Chim. Fr. 1964, 407.

15. P. K. Grant and M.H.G. Munro, Tetrahedron Lett. 1965, 3729.
16. P. S. Rao, G. P. Suchder, T. R. Seshadri, and H. B. Singh, Tetrahedron Lett. 1968, 4685.
17. T. G. Quesada, B. Rodriguez, and S. Valverde, Tetrehedron Lett. 1972, 2187.
18. W. Dadziel, B. Hesp, K. M. Stevenson, and J.A.J. Jarvis, J. Chem. Soc. (Perkin Trans. I) 1973, 2841.
19. P. R. Jeffries and T. Ratajczak, Aust. J. Chem. 1973, 26, 173.
20. Y. Tsuda, T. Sano, A. Morimoto, M. Hatanaka and Y. Inubushi, Chem. Pharm. Bull. (Tokyo) 1975, 23, 1290.
21. Y. Tsuda, T. Sano, K. Isobe and M. Miyauchi, Chem. Pharm. Bull. (Tokyo) 1974, 22, 2396.
22. Y. Tsuda, T. Sano, K. Isobe and M. Miyauchi, Chem. Pharm. Bull. (Tokyo) 1975, 23, 1336.
23. Y. Tsuda, K. Isobe and T. Sano, Chem. Pharm. Bull. (Japan) 1975, 23, 264.
24. A. H. Conner and J. W. Rowe, Phytochemistry 1977, 16, 1777.
25. J. P. Kutney, G. Eigendorf and I. H. Rogers, Tetrahedron Lett. 1969, 3753.
26. K. Tori, S. Seo, S. Shimaoko and Y. Tomita, Tetrahedron Lett. 1974, 4227.
27. S. Seo, Y. Tomita and K. Tori, Tetrahedron Lett. 1975, 7.
28. F. Khuong-Huu, M. Sangare, V. M. Chari, A. Bekaert, M. Devys, M. Barbier and G. Lukacs, Tetrahedron Lett. 1975, 1787.
29. P. Crews and E. Kho-Wiseman, Tetrahedron Lett. 1978, 2483.
30. J. W. Blunt and M.H.G. Munro, Org. Magn. Reson. 1980, 13, 26.
31. Y. Tsuda and M. Hatanaka, J. Chem. Soc. (Chem. Comm.) 1969, 1041.
32. Y. Inubushi, T. Hibino, T. Harayama, T. Hasegawa and R. Somanathan, J. Chem. Soc. C 1971, 3109.
33. T. P. Harmony and M. Sundaralingam, Acta Cryst. 1982, B38, 1365.
34. Y. Tsuda, T. Sano, A. Morimoto and Y. Inubushi, Y. Tetrahedron Lett. 1966, 5933.
35. R. G. Curtis, I. Heilborn, E.R.H. Jones and G. F. Woods, J. Chem. Soc. (London) 1953, 457 and 461.

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