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TERPENOIDS OF THE RED ALGA *LAURENCIA PINNATIFIDA*[1)]

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Abstract - The structures of three brominated terpenoids which are natural products from the red alga *Laurencia pinnatifida* (Gmal. Lamour) are described. The structures of the sesquiterpenes 4 and 5 were determined by spectral comparison and chemical interconversion. The structure of the squalene-derived terpenoid 8 was secured by chemical transformation into thyrsiferol, a brominated triterpene previously isolated from the red alga *Laurencia thyrsifera*.

As part of a program aimed at assessing the diversity of halogen-based secondary metabolite synthesis in the red seaweed *Laurencia* (Rhodomelaceae), we have investigated the metabolites from a number of unrecorded species from this genus indigenous to the Canary Islands[2)]. In a previous work with ether extracts of the *L. pinnatifida* (Gmal. Lamour)[3)], we have isolated a variety of compounds including the two halogenated ethers, *cis*-pinnatifidenyne (1) and *trans*-pinnatifidenyne (2), and the acyclic trienyne (3). These compounds are representative of a group of related ethers of algal origin characterized by a straight-chain C_{15} carbon skeleton and a terminal enyne functionality[4)]. In addition, we have been actively investigating several terpenoid compounds known to be characteristic components of many *Laurencia* species. In this paper we wish to describe the structures of three new terpenoids which are related to the previously described natural products, isolaurinterol[5)] and thyrsiferol[6)].

Hexane, ether and acetone extracts of powdered, air-dried *Laurencia pinnatifida* were combined to yield a viscous oil (1.3% dry weight) which was chromatographed on silica gel, using a solvent gradient of increasing polarity from n-hexane to ethyl acetate. Selected fractions were rechromatographed to obtain individual compounds, of which *cis*-pinnatifidenyne (1) (0.12% dry weight) was again the major metabolite.

The least polar sesquiterpene metabolite was the non-aromatic triene (4), which was isolated as an unstable, colourless oil, $\{\alpha\}_D$+2.3 (c, 2.15, $CHCl_3$). The high-resolution mass spectrum established the molecular formula $C_{15}H_{21}Br$. The structure 4 followed from the ^{1}H- and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum of (4) indicated the presence of two methyl singlets at 1.15 and 1.64, together with four vinyl protons at 4.86 (1H, *d*, *J*= 2.3Hz) and 5.04 (1H, *d*, *J*= 1.9Hz), corresponding to an exocyclic methylene grouping, and 5.40, 5.56 (1H each, *bs*) ascribed to the non-conjugated cyclohexadiene system. The remaining signals at 2.57 (4H, *bs*) due to C_8 and C_{11} protons, an ABX system at 2.95 (1H, *m*), 3.23 (1H, *dd*, *J*= 10.4, 9.5Hz), and 3.53 (1H, *dd*, *J*= 9.5, 4.7Hz) were assigned to C_3, C_{12} protons. Irradiation of the methine multiplet at 2.95 caused the bromomethylene signals at 3.23 and 3.53 to collapse to doublets, and the exocyclic methylene protons at 4.86 and 5.04 to collapse to singlets. The ^{13}C-NMR data for 4, assisted by off-resonance and selective proton-noise decoupling techniques showed the presence of two methyls, 22.85 (C_{15}), 26.71 (C_{14});

six methylenes, 26.45 (C_{11}), 29.35 (C_4), 32.22 (C_8), 36.61 (C_5), 38.47 (C_{12}), 109.14 (C_{13}); three methines, 47.14 (C_3), 119.19 (C_{10}), 119.51 (C_7), and four fully-substituted carbon atoms, 52.13 (C_1), 130.92 (C_9), 138.47 (C_6), 159.08 (C_2).

Compound 5 was isolated as a colourless oil, $\{\alpha\}_D$+4.7 (c, 3.19, $CHCl_3$). Mass spectral analysis gave a molecular formula of $C_{15}H_{19}Br$, indicating six degrees of insaturation. The ^{1}H-NMR spectrum of 5 showed signals due to an aromatic methyl group at δ2.33, four aromatic protons at 7.26 and 7.20 (each 2H, *d*, *J*= 8.3Hz). The remaining signals at δ1.42, due to the tertiary methyl group, 3.19 (1H, *dd*, *J*= 10.4, 9.2Hz), 3.58 (1H, *dd*, *J*= 9.2, 4.4Hz), due to the bromo-methylene protons; and 5.05 (1H, *d*, *J*= 2.1Hz), 5.24 (1H, *d*, *J*= 1.8Hz), due to the exocyclic methylene protons, were remarkably similar to those observed for compound 4. The ^{13}C-NMR data showed the presence of two methyls, 20.97 (C_{15}), 29.71 (C_{14}); four methylenes, 29.20 (C_4), 38.47 (C_{12}), 40.46 (C_5), 110.20 (C_{13}); five methines, 47.32 (C_3), 126.55 (C_7 and C_{11}), 129.02 (C_8 and C_{10}), 144.44 (C_6), 159.88 (C_2). The stereochemical relationship between 4 and 5 was indicated by the ^{1}H- and ^{13}C-NMR spectra and was established by the conversion of 4 into 5 on standing or by refluxing a solution of 4 in toluene and a catalytic amount of palladium on charcoal.

The remaining sesquiterpenes isolated were identified with the previously reported ethers: compound 6[7] and compound 7[8]. Dehydrothyrsiferol (8) was isolated as a pure, crystalline substance (needles from acetone, mp 103-104°, $\{\alpha\}_D$-203 (c, 0.64, $CHCl_3$). The molecular formula was determined as $C_{30}H_{51}BrO_6$ by mass measurement of the $|M^+-HBr|$ peak, as the molecular ion doublet corresponding to M^+ at *m/z* 588, 586 was of low intensity. The IR spectrum (ν_{max}^{KBr} 3450, 3100, 1640, 1450, 1370, 1100 and 890 cm^{-1}).

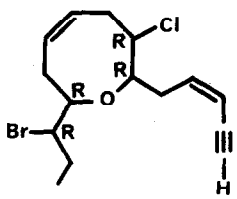
The ^{1}H-NMR spectrum exhibits in the lowfield region signals for nine protons at: 5.04 (1H, *bs*), 4.88 (1H, *bs*), 4.28 (1H, *dd*, *J*= 8 and 4.5Hz), 3.89 (1H, *dd*, *J*= 12.5 and 4.5Hz), 3.75 (1H, *dd*, *J*= 10 and 7Hz), 3.51 (1H, *dd*, *J*= 10 and 2.5Hz), 3.42 (1H, *dd*, *J*= 12 and 6.5Hz), 3.08 (1H, *dd*, *J*= 11.5 and 2.5Hz), 2.46 (1H, *ddd*, *J*= 12, 8.5 and 5Hz); from 2.30 to 1.40 appear signals covering for nineteen protons. In the upfield region appear signals for seven tertiary methyl groups at 1.39, 1.27, 1.22, 1.21, 1.18, 1.13 and 1.11 (3H each, *s*).

The ^{13}C-NMR spectrum showed the presence of seven methyls at 19.61, 20.12, 23.64, 23.67, 24.02, 27.61, 31.01; eleven methylenes, 21.83, 22.99, 26.35, 26.60, 28.28, 29.48, 30.10, 31.90, 37.03, 38.76, 109.83; six methines, 58.98, 72.56, 76.31, 78.81, 86.71, 87.63; and six fully-substituted carbon atoms, 70.49, 72.80, 74.44, 74.97, 86.06, 151.43. The ^{13}C-NMR spectrum confirmed that compound 8 was highly oxygenated as ten carbon-oxygen, besides the carbon-bromine, type resonances were discernible.

The non-carbocyclic, although tetracyclic nature of 8, and the presence of four ether bridges, were demonstrated from the absence of further unsaturation beside the methylenic moiety, and from the chemical clarification of two of the oxygen atoms. Compound 8 gave the hydroxy-monoacetate 9 by treatment with Ac_2O/Py, and the monobenzoate 10 by reaction with benzoyl chloride/Py at r.t. Upon oxidation with chromic anhydride-pyridine complex, compound 8 yielded the hydroxy-ketone 11, which is indicative of a secondary hydroxyl and the tertiary nature of the non-acylable hydroxy group. The epimeric mixture of the epoxides 12 was obtained in 98% yield by treatment of 8 with m-chloroperbenzoic acid-potassium fluoride complex[9] in methylene chloride. The hydride reduction of 12 with LAH in THF at -75° gave the 3:1 mixture of the triols 13 and 14. After acetylation with Ac_2O/Py, compound 14 gave the dihydroxy monoacetate 15 which was shown to be identical in all respects with thyrsiferol monoacetate[10], a squalene-derived metabolite isolated from the same genus of alga *L. thyrsifera*[6].

EXPERIMENTAL

Mps were determined on a Kofler block and are uncorr. Infrared spectra were recorded on Perkin-Elmer Mod. 237 and Mod. 681 spectrophotometers and ultraviolet spectra recorded on a Perkin-Elmer Mod. 137 or a Unicam SP800. Optical rotations were determined for solutions in chloroform with a Perkin-Elmer 141 polarimeter. ^{1}H-NMR spectra were recorded on Perkin-Elmer R-32 (90MHz) and Brucker Mod. WM 360 spectrometers, chemical shifts are reported relative to Me_4Si (δ0) and coupling constants are given in hertz. ^{13}C-NMR spectra were obtained on a Brucker Mod. WM 360 and the chemical shifts are reported relative to Me_4Si (δ0). Low and high resolution mass spectra were obtained from a VG Micromass ZAB-2F. Column and dry column chromatography were performed on silica gel 0.2-0.5 and 0.005-0.2 mm, respectively, and TLC and PLC on silica gel G, all Merck products. The TLC plates were developed by spraying with 6N-sulphuric acid and heating. All solvents were



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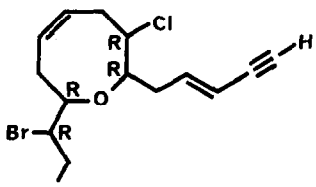

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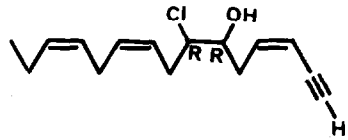

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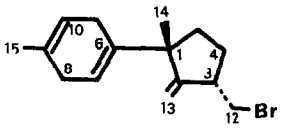

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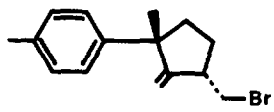

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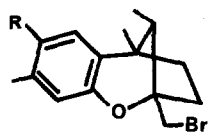
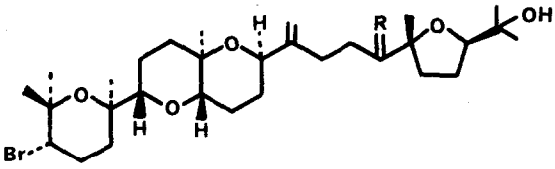
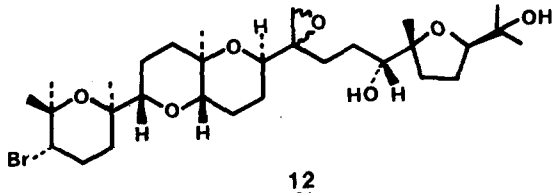


6 R=H
7 R=Br



8 R,---OH, —H
9 R,---OAc, —H
10 R,---OBz, —H
11 R,= O



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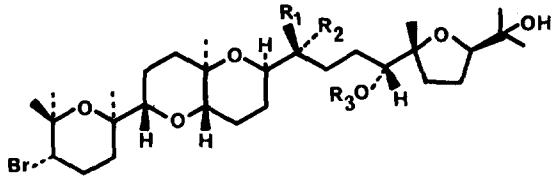

13 $R_1=CH_3$, $R_2=OH$, $R_3=H-$
14 $R_1=OH$, $R_2=CH_3$, $R_3=H-$
15 $R_1=OH$, $R_2=CH_3$, $R_3=Ac-$

purified by standard techniques. Anhydrous sodium sulphate was used for drying solutions.

Collection, extraction and chromatographic separation

Laurencia pinnatifida was collected in April-May 1980, by hand, using SCUBA (-2 to -10 m) near Los Cristianos, Tenerife; air-dried and ground in a Wiley mill to a 1 mm particle size. The dried alga (10.2 kg) was extracted in a Soxhlet apparatus for 24 h each with hexane (5 L), diethyl ether (5 L), and acetone (5 L). The combined extracts were evaporated to leave a dark-green viscous oil (140.5 g, 1.3% dry weight). The crude extract (140.5 g) was added as a concentrated n-hexane solution to a column (90 x 7 cm) containing silica gel (950 g) in n-hexane. One-litre fractions were collected employing the following elution scheme: hexane, fractions 1-15; hexane/ethyl acetate (20/1), fractions 16-24; hexane/ethyl acetate (20/3), fractions 25-32; hexane/ethyl acetate (20/6), fractions 33-47; hexane/ethyl acetate (1/1), fractions 48-53; ethyl acetate, fractions 54-61. Fractions exhibiting similar tlc profiles were combined. A portion of 7.5 g of combined fractions 2-10 (27 g) was chromatographed on 120 g of silica gel H using n-hexane as solvent and collecting 20-ml fractions. Fractions 2-4 yielded compound 4 (18 mg); fractions 6-9 yielded compound 5 (21 mg). Fractions 10-23 (680 mg) were rechromatographed on a column (30 x 2 cm) of silica gel (35 g) in n-hexane, yielding a mixture of bromo-ethers (260 mg) which was separated by PLC using 1% diethyl ether in petroleum ether as an eluent to obtain 6 (128 mg, 0.012%) and 7 (132 mg, 0.014%).

Fractions 32-44 (2.3 g) were rechromatographed on a column (30 x 1.5 cm) containing silica gel (25 g) in 5% ethyl acetate in n-hexane, which allowed isolation of dehydrothyrsiferol (8) (1.12 g, 0.11%).

Compound 4: was isolated as an oil, $[\alpha]_D$+2.3 (c, 2.15, $CHCl_3$); IR (neat) 3065, 3020, 1640, 1510, 1445, 1360, 1155, 950, 890, 880 and 815 cm^{-1}. High resolution mass measurement observed 280.0823, $C_{15}H_{21}{}^{79}Br$ requires 280.0827. Significant peaks in the mass spectrum appeared at *m/z* (relative intensity) 203(3); 189(2); 185, 187(1:1)(3); 157(6); 145(11); 141(12); 131(14); 119(25); 115(42); 107(21); 105(43); 95(41); 91(100); 79(33).

Compound 5: was isolated as an oil, $[\alpha]_D$+4.7 (c, 3.19, $CHCl_3$); IR (neat) 3070, 1640, 1622, 1577, 1504, 1411, 1160, 1240, 1167, 1080, 965, 860 and 811 cm^{-1}. High resolution mass measurement, observed 278.0665, $C_{15}H_{19}{}^{79}Br$ requires 278.0671. Significant peaks in the mass spectrum appeared at *m/z* (relative intensity) 265(4); 237, 239(1:1)(3); 225(3); 210, 212(1:1)(15); 199(18); 185(12); 155, 157(1:1)(10); 145(18); 128(25); 115(32); 105(20); 93(15); 81(18).

Bromoether 6: was isolated as a crystalline compound; mp 74-75°, $[\alpha]_D$+23.2 (c, 1.27, $CHCl_3$) having spectral properties identical with those reported[7] for the laurenisol rearranged bromoether 6. ^{13}C-NMR ($CDCl_3$) 152.6 (*s*), 137.6 (*s*), 127.3 (*s*), 125.0 (*d*), 121.5 (*d*), 116.1 (*d*), 85.9 (*s*), 45.2 (*s*), 44.5 (*d*), 42.0 (*t*), 36.6 (*t*), 34.7 (*t*), 21.1 (*q*), 20.6 (*q*), 7.3 (*q*) ppm.

Dibromoether 7: was isolated as a crystalline compound; mp 88-89°, $[\alpha]_D$+22.5 (c, 1.18, $CHCl_3$) having spectral properties identical with those reported[8] for the dibromoether 7. ^{13}C-NMR ($CDCl_3$) 130.0 (*s*), 128.7 (*d*), 117.8 (*d*), 86.2 (*s*), 45.4 (*s*), 44.3 (*d*), 41.8 (*t*), 36.3 (*t*), 34.7 (*t*), 22.6 (*q*), 20.5 (*q*), 7.3 (*q*) ppm.

Dehydrothyrsiferol (8): was isolated as a crystalline substance; mp 103-104°, $[\alpha]_D$-203 (c, 0.64, $CHCl_3$). IR ν_{max}^{KBr} 3450, 3100, 1640, 1450, 1370, 1320, 1245, 1220, 1125, 1100, 1060, 990, 960, 940 and 890 cm^{-1}. High resolution mass measurement, observed 506.3606, $C_{30}H_{50}O_6$ (M^+-HBr) requires 506.3607. Significant peaks in the mass spectrum appeared at *m/z* 443, 445 ($M^+-C_8H_{16}O_2$); 363 $|M^+-(C_8H_{16}O_2|$+ HBr); further peaks at *m/z* (relative intensity) 291(4); 234(3); 221(5); 151, 153 (1:1)(20); 193(4); 106(10); 96(100); 78(87).

Acetylation of the diol 8: The diol 8 (18 mg) was dissolved in a mixture of acetic anhydride (1 ml) and pyridine (2 ml) and the resulting solution was stirred for 16 h at room temperature. The reagents were removed *in vacuo* and the residue was purified on a silica gel plate (20 x 20 x 0.025 cm) using diethyl ether as eluent to obtain the monoacetate 9 (17 mg) as an oil: IR ($CHCl_3$) 3550, 2980, 1725, 1640, 1445, 1375, 1225, 1095 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ5.05 (1H, *dd*, *J*= 10, 4.5Hz); 5.03 (1H, *bs*); 4.86 (1H, *bs*); 4.50-2.50, signals covering for five protons; 2.05, 1.40, 1.24 (*s*, 3H each), 1.19 (*s*, 12H), 1.10 (*s*, 3H); mass spectrum *m/z* (relative intensity) 548(2) (M^+-HBr); 289, 291(1:1)(1); 207(6); 153(2); 143(19); 135(2); 125(22).

Benzoylation of the diol 8: The diol 8 (19 mg) was dissolved in a mixture of benzoyl chloride (0.5 ml) and pyridine (1 ml) and the resulting solution treated according to the previous procedure (except 30% ether in hexane) to obtain the monobenzoate 10 (12 mg) as an oil, $[\alpha]_D$-125 (c, 0.32, $CHCl_3$); IR ($CHCl_3$) 3550, 2980, 1740, 1645, 1440, 1225 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ8.03-7.51 (*m*, 5H), 5.11 (1H, *dd*, *J*= 10, 3.5Hz), 4.95 (1H, *s*), 4.84 (1H, *s*), 4.15 (2H, *m*), 3.75 (3H, *m*), 3.28 (1H, *dd*, *J*= 12, 7Hz), 2.98 (1H, *m*), 1.36 (3H, *s*), 1.25 (6H, *s*), 1.15, 1.12, 1.06, 1.01 (*s*, 3H each). Mass spectrum *m/z* (relative intensity) 610(7) (M^+-HBr); 551(2); 468(1); 289, 291(1:1)(4); 247(2); 169, 171(12); 143(100).

Oxidation of dehydrothyrsiferol (8) to hydroxyketone 11: Dehydrothyrsiferol (8) (30 mg, 0.06 mmol) was dissolved in dichloromethane (4 ml) and stirred at 25°C. A solution of the pyridine complex of chromic oxide (0.36 mmol) in dichloromethane (0.9 ml) was added dropwise, and the resulting mixture was stirred for 15 min at 25°C. Water (5 ml) was added, and the organic material was extracted with dichloromethane (2 x 10 ml). The combined organic extracts were dried over sodium sulphate and the solvent evaporated to leave a brown oil (27 mg) which was purified by preparative tlc on silica gel (20 x 20 x 0.025 cm) using 10% diethyl ether in hexane as an eluent to obtain the hydroxyketone 11 as an oil; IR (neat) 3550, 2980, 1710, 1640, 1450, 1370, 1320 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 5.02 (1H, *bs*), 4.88 (1H, *bs*), 4.30 (1H, *dd*, *J*= 9, 4.5Hz), 4.00-2.50, signals covering for five protons; 1.40, 1.26 (*s*, 3H each), 1.22 (*s*, 6H), 1.18, 1.12, 1.11 (*s*, 3H each). Mass spectrum *m/z* (relative intensity) 504(4) (M^+-HBr); 287, 289(1:1)(3); 205(10); 153(4); 143(100).

Epoxidation of dehydrothyrsiferol (8) to epoxy-epimers 12: Dehydrothyrsiferol (500 mg, 0.85 mmol) and sodium acetate (1.70 mmol) were dissolved in dichloromethane (5 ml) and the solution stirred at 25°C for 30 min. A solution of the 1:1 complex of potassium fluoride-m-chloroperbenzoic acid (1.70 mmol) in dichloromethane (5 ml) was added dropwise under nitrogen and the resulting mixture was stirred at 25°C for 12 h. The reaction mixture was poured into ice, extracted with dichloromethane and worked up as usual. Recrystallization of the resulting solid (490 mg) gave 12 as colourless crystals; mp 88-90°. IR (KBr) 3550, 2980, 1470, 1455, 1225 cm^{-1}. ^{1}H-NMR ($CDCl_3$) 3.80 (1H, *dd*, *J*= 12, 3Hz); 3.68 (1H, *dd*, *J*= 12, 5.5Hz); 3.45 (2H, *m*); 2.95 (1H, *bd*, *J*= 9Hz); 2.70 (2H, *m*); 2.60 (1H, *bs*); 1.31, 1.18, 1.17, 1.12, 1.11 (*s*, 3H each), 1.05 (*s*, 6H). High resolution mass measurement, observed 522.3541, $C_{30}H_{50}O_7$ (M^+-HBr) requires 522.3543. Significant peaks in the mass spectrum appeared at *m/z* (relative intensity) 380(2), 296(3), 279(5), 261(2), 247(2), 243(7), 225(7), 221(3), 211(4), 209(7), 207(6), 205(3), 193(5), 143(100).

Reduction of 12 to the triols 13 and 14: A solution of the epoxide 12 (490 mg, 0.81 mmol) in dry tetrahydrofuran (5 ml) was added to a stirred suspension of lithium aluminium hydride (50 mg, 1.5 mmol) in dry THF at -78°C. After 15 min, the reaction mixture was warmed to -5°C and allowed to stir for an additional 30 min. Ethyl acetate (1 ml) was added cautiously, followed by water (0.5 ml), 3N potassium hydroxide solution (0.5 ml) and water (1.0 ml). The precipitate was removed by filtration and washed with ether (3 x 10 ml). The combined extracts were dried over magnesium sulfate and the solvent evaporated to yield a solid (354 mg). The residue was applied to one preparative plate and this was eluted three times with light petroleum-diethyl ether (2:1). The less polar band offered the triol 13 as a crystalline solid (120 mg); mp 158-160°, $[\alpha]_D$+10.0 (c, 0.62, $CHCl_3$). IR (CCl_4) 3550, 3400, 2980, 1450, 1370, 1340, 1235, 1120, 1100, 1020 cm^{-1}. ^{1}H-NMR ($CDCl_3$) 3.93 (1H, *dd*, *J*= 9, 3Hz); 3.80-3.40 (4H, *m*); 3.11 (1H, *bd*, *J*= 5Hz); 2.65 (1H, *bs*); 1.42, 1.30, 1.23, 1.22, 1.21, 1.18, 1.16, 1.14 (*s*, 3H each). ^{13}C-NMR ($CDCl_3$) 87.76 (*d*), 86.71 (*d*), 77.57 (*d*), 76.50 (*d*), 76.21 (*s*), 75.19 (*s*), 75.12 (*s*), 74.55 (*s*), 73.52 (*s*), 72.09 (*d*), 70.67 (*s*), 59.08 (*d*), 38.71 (*t*), 37.15 (*t*), 36.25 (*t*), 32.08 (*t*), 31.16 (*q*), 28.40(*t*), 27.74 (*q*), 26.76 (*t*), 25.63 (*t*), 24.13 (*q*), 23.84 (*q*), 23.50 (*t*), 23.17 (*t*), 21.54 (*q*), 21.22 (*q*), 21.07 (*t*), 20.95 (*q*), 20.94 (*q*). High resolution mass measurement, observed 524.3697, $C_{30}H_{52}O_7$ (M^+-HBr) requires 524.3699. Significant peaks in the mass spectrum appeared at *m/z* (relative intensity) 523(3); 506(2); 398(2); 363(6); 319(3); 279(6); 234(4); 227(46); 221(5); 209(40); 205(5); 195(3); 193(7); 155(10); 143(100); 125(95); 111(11). The second band offered the triol 14 as a non-crystalline solid (38 mg), $[\alpha]_D$ +6.8 (c, 0.16, $CHCl_3$); IR (CCl_4) 3600, 3550, 3020, 1460, 1360, 1210, 1120, 1100, 1060 and 890 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ3.95 (1H, *dd*, *J*= 9, 4Hz); 3.80-3.40 (4H, *m*), 3.15 (1H, *bd*, *J*= 5.5Hz); 1.45, 1.32,

1.30, 1.26, 1.25, 1.23, 1.21, 1.18 (*s*, 3H each). ^{13}C-NMR ($CDCl_3$) 87.44 (*d*), 86.51 (*d*), 86.03 (*s*), 77.63 (*d*), 76.31 (*d*), 76.07 (*s*), 74.93 (*s*), 74.35 (*s*), 73.23 (*s*), 71.95 (*d*), 70.54 (*s*), 58.98 (*d*), 38.51 (*t*), 37.03 (*t*), 33.53 (*t*), 32.36 (*t*), 31.00 (*q*), 28.21 (*t*), 27.65 (*q*), 26.58 (*t*), 25.46 (*t*), 23.93 (*q*), 23.67 (*q*), 23.38 (*q*), 22.97 (*t*), 22.90 (*t*), 21.42 (*q*), 21.13 (*t*), 20.68 (*q*), 20.05 (*q*). High resolution mass measurement, observed 524.3698, $C_{30}H_{52}O_7$ (M^+-HBr) requires 524.3699. Significant peaks in the mass spectrum appeared at *m/z* (relative intensity) 488(2); 403(1); 398(2); 380(2); 363(6); 361(1); 319(3); 306(2); 296(3); 279(6); 261(2); 243(4); 234(4); 227(51); 221(5); 209(40); 204(1); 195(3); 191(5); 183(4); 165(5); 156(10); 143(100); 127(30); 125(95). The triol 14 was treated with Ac_2O/Py at room temperature overnight, to yield the monoacetate 15 which was crystallized from acetone giving needles, mp 105°, $[\alpha]_D$+12.2 (c, 0.18, $CHCl_3$). The physical and spectroscopic data (tlc, glc, IR, ^{1}H-NMR, MS) were identical with those reported for thyrsiferol monoacetate[6,10].

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