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LONGIFOL-7(15)-EN-5β-OL AND LONGIFOLAN-3α,7α-OXIDE: NEW SESQUITERPENES FROM JUNIPERUS CONFERTA PARL.

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In the previous papers[1,2,3] we reported the constituents of the heartwood extractive of *Juniperus conferta* Parl., including sesquiterpenes, diterpenes and tropolones. The present communication reports the isolation and characterization of further two new sesquiterpenes, longifol-7(15)-en-5β-ol(I) and longifolan-3α,7α-oxide(VI), from the same plant.

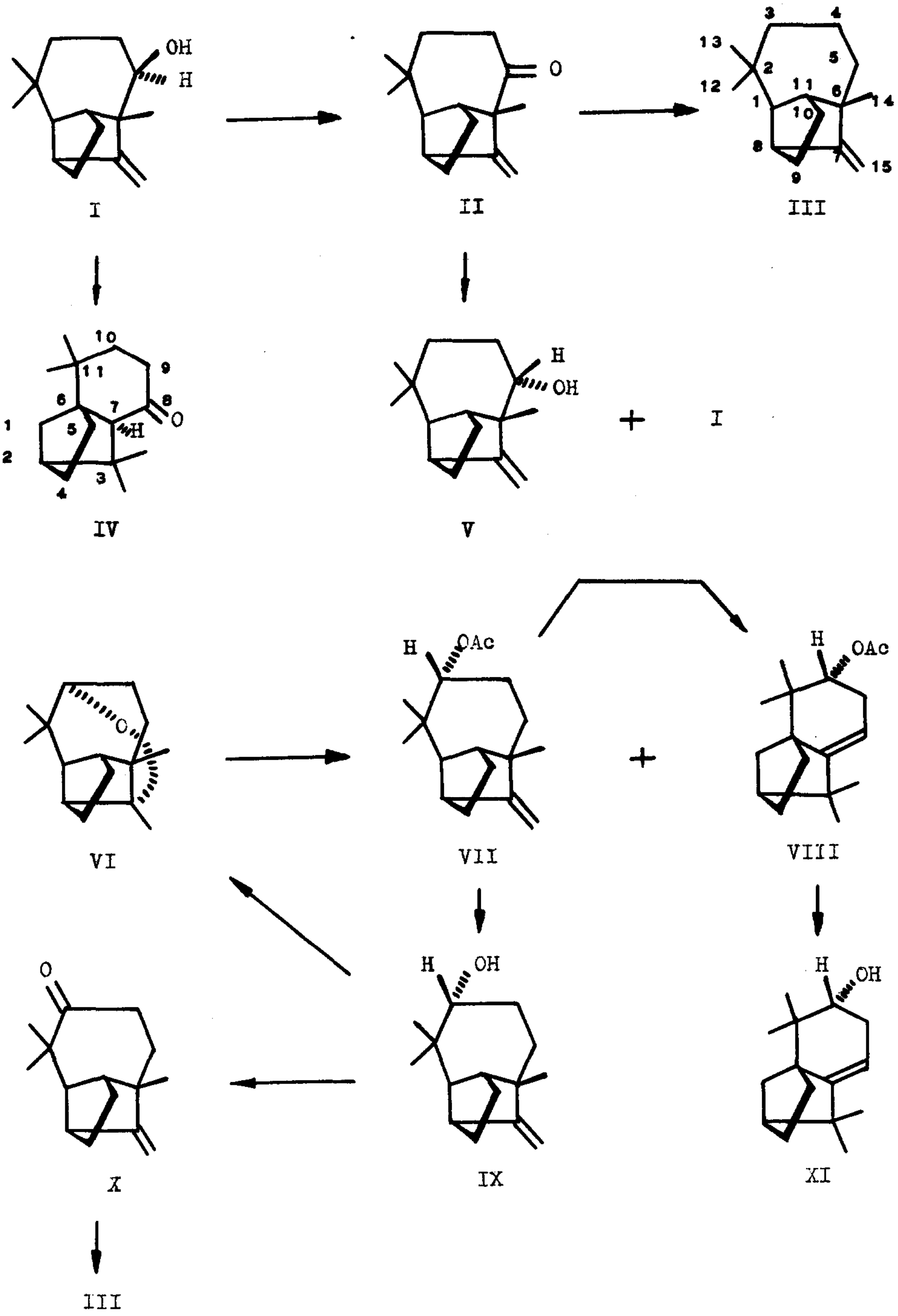
The alcohol(I), $C_{15}H_{24}O$(MS), m.p.86-87°, $[\alpha]_D^{11}$ +13.5°($CHCl_3$), $\nu_{max}^{KBr}(cm^{-1})$: 3300,1015($-\overset{|}{C}HOH$),3070,1655,873($-\overset{|}{C}=CH_2$), $\delta_{CCl_4}^{TMS}$(ppm): 0.88(s,CH_3), 0.96(s,CH_3), 1.06(s, 14-CH_3), 3.50(double t, $-CH_2\overset{|}{C}\underline{H}OH$, J=6.7 and 1.7 Hz), 4.40 and 4.73 (each s, $-\overset{|}{C}=CH_2$), resembles closely in its spectral behaviors longifolene(III) except the additional hydroxyl. In fact, I was oxidized with Cornforth reagent[4] to the corresponding ketone(II), $C_{15}H_{22}O$(MS), b.p.85°/5(bath), $[\alpha]_D^{16}$ +52.7°, ν^{liq}: 1692,1412($-CH_2CO-$), 3050,1656,882($-\overset{|}{C}=CH_2$), δ : 0.99(s, 2×CH_3), 1.16(s,CH_3), 2.31(m, $-CH_2CO-$), 4.51 and 4.77(each s, $-\overset{|}{C}=CH_2$), followed by Huang-Minlon reduction to yield III. On a mild treatment with BF_3 in benzene I rearranged to 8-oxo-isolongifolane (IV), $C_{15}H_{24}O$(MS), identical with an authentic sample[5] by direct comparisons of their IR and NMR spectra. These facts as well as proposed mechanism of the acid-catalyzed isomerism of longifolene to isolongifolene[5] establish the structure of the alcohol (I).

The ketone(II), on reduction with $NaBH_4$ in ethanol, afforded I and epimeric longifol-7(15)-en-5α-ol(V), $C_{15}H_{24}O$(MS), m.p.34-35°, $[\alpha]^{19}_{D}$ +26.6°, ν : 3450,,1010($-\overset{|}{C}HOH$), 3080,1646,885($-\overset{|}{C}=CH_2$), δ:0.92(s,CH_3),0.93(s,CH_3), 1.15 (s, 14-CH_3),3.45(t, $-CH_2\overset{|}{C}\underline{H}OH$, J=3.0 Hz), 4.65 and 4.78(each s, $-\overset{|}{C}=CH_2$)(ratio of formation of I to V=1:4). Taking into account of a Dreiding model of II, solvated borohydride ion should attack the carbonyl predominantly in front of the less hindered β-side, implying the hydroxyl of the major product(V) of the reduction is α-orienting and thus the minor (I) β.

On the other hand, the chemical shifts of 14-CH_3 and 5-H of I and V in pyridine solution were found in δ-values at 1.36s, 3.83m and 1.35s, 3.74m, respectively. Undoubtedly, the solvent-induced shifts($\delta_{CCl_4} - \delta_{pyridine}$) affect much more in I than in V, providing an additional evidence for the proposed orientation of the hydroxyl of I.

The sesquiterpene oxide(VI), $C_{15}H_{24}O$(MS), m.p.33-34°, $[\alpha]^{20}_{D}$ -144.8°, ν: 1097,1050,1036, δ: 0.81(s,CH_3), 0.87(s,CH_3), 0.96(s,CH_3), 1.10(s, CH_3), 3.36 (m, $-\overset{|}{\underset{|}{C}}-O-\overset{|}{C}H-$), yielded on a mild treatment with BF_3 in acetic anhydride a mixture of the two acetates which were separated by $AgNO_3$-impregnated silica-gel chromatography into 3α-acetoxylongifolene(VII), $C_{17}H_{26}O_2$(MS), b.p.90°/1 (bath), $[\alpha]^{14}_{D}$ +63.0°, ν^{liq}: 1745,1254($-OCOCH_3$), 3050,1668,882($-\overset{|}{C}=CH_2$), δ:0.90 (s, 2×CH_3), 1.02(s,CH_3), 1.83(s, $-OCOCH_3$), 4.32 and 4.70(each s, $-\overset{|}{C}=CH_2$), and 10α-acetoxy-isolongifolene(VIII), $C_{17}H_{26}O_2$(MS), m.p.52-53°, $[\alpha]^{14}_{D}$ -97.9°, ν: 1720,1245($-OCOCH_3$), 830($-\overset{|}{C}=\overset{|}{C}H-$), δ: 0.88(s, 2×$CH_3$),0.95(s,$CH_3$), 1.03(s, CH_3), 1.94(s, $-OCOCH_3$),4.77(q, $-CH_2\overset{|}{C}\underline{H}OCOCH_3$, J=6.0 Hz),4.98(q, $-CH_2C\underline{H}=\overset{|}{C}-$, J=2.0 Hz).

The former acetate(VII) was converted with $LiAlH_4$ in ether into the corresponding alcohol(IX), $C_{15}H_{24}O$(MS), m.p.50-52°, $[\alpha]^{22}_{D}$ -113.5°, ν :3500, 1070($-\overset{|}{C}HOH$), 3060,1650,875($-\overset{|}{C}=CH_2$), δ: 0.97(s, 2×CH_3), 1.06(s, CH_3), 3.15 (broad s, $-\overset{|}{C}HOH$), 4.65 and 4.89(each s, $-\overset{|}{C}=CH_2$), which was transformed by oxidation with Cornforth reagent to the ketone(X), $C_{15}H_{22}O$(MS), m.p.35-36°, $[\alpha]^{25}_{D}$ 0°, ν: 1708,1410($-COCH_2-$), 3070,1660,880($-\overset{|}{C}=CH_2$), δ : 0.97(s, CH_3), 1.07(s, CH_3), 1.16(s,CH_3), 2.35(m, $-COCH_2-$), 4.50 and 4.71(each s, $-\overset{|}{C}=CH_2$), followed by Huang-Minlon reduction to give longifolene(III).


OH
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OAc
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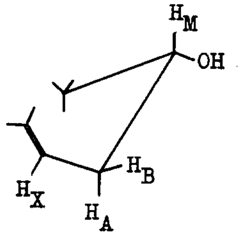
O
VI
VII
+
H
OAc
VIII
H
OH
O
X
IX
H
OH
XI
III

These facts demonstrate not only the longifolane skeleton of the oxide (VI) but also the location of the hydroxyl of the alcohol (IX) because of a down-field shift of 13β-methyl signal at δ 0.97 in IX to δ 1.16 in X due to deshielding effect of the carbonyl. On the other hand, the alcohol (IX) was readily converted back to the original oxide (VI) even on being merely heated in chloroform, providing an additional support for the proposed positions of both terminals of the oxide ring of VI.

The latter acetate (VIII), obtainable also directly from VII by a similar treatment with BF_3 in acetic anhydride, afforded on alkaline hydrolysis the alcohol (XI), $C_{15}H_{24}O$ (MS), m.p.107-109°, $[\alpha]_D^{16}$ -128.2°, ν : 3250,1080 ($-\overset{|}{C}HOH$), 818 ($-\overset{|}{C}=CH-$). As shown in the following table, its NMR other than four methyls (δ: 0.78, 0.96, 0.96, 1.02, all s) suggests that XI possesses the partial structure of XII, establishing the orientations of the hydroxyls of XI and IX, and successively of the oxide ring of VI.



XII

	δ				
H_A	1.92 dd	J_{AM}	9.7 Hz	J_{AX}	3.0 Hz
H_B	2.08 dd	J_{BM}	6.0 Hz	J_{BX}	4.5 Hz
H_M	3.56 dd				
H_X	4.95 dd				

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