Constituents of *Solidago* Species. Part III.[1] The Constitution of Diterpenoids from *Solidago juncea* Ait.

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The constitution and stereochemistry of five new diterpenoids from *Solidago juncea* Ait., junceic acid (3*a*), the related epoxide (6*a*), junceanol W(4*a*), junceanol X (4*b*), and junceanol Y (5*a*), have been assigned on the basis of their chemical and spectroscopic properties. Of key importance in these deductions have been the transformations of 4*b* and 5*a* into the previously described hydrocarbon **19** and of 3*a* into 3*e*. Two known diterpenoids, (−)-hardwickiic acid (2*a*), which has also been converted into 3*e*, and *ent*-16-kauren-19-oic acid (**1**), are further constituents of *S. juncea.*

La constitution ainsi que la stéréochimie de cinq nouveaux diterpènes issus du *Solidago juncea* Ait., l'acide junceique (3*a*), l'époxyde parent (6*a*), le junceanol W(4*a*), le junceanol X (4*b*) et le junceanol Y (5*a*) ont été attribuées en se basant sur les propriétés chimiques et spectroscopiques. Les transformations de 4*b* et 5*a* pour donner l'hydrocarbure **19** décrit antérieurement et de 3*a* en 3*e* ont été de la plus grande importance dans ces déductions. Deux diterpènes connus, l'acide (−) hardwickiique (2*a*) qui a aussi été transformé en 3*e* et l'acide kauren-16-*ent* oique-19 sont aussi d'autres constituants du *S. juncea*.

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Continuing our investigations of the constituents of *Solidago* species we have examined two samples of *S. juncea* Ait. (Early Goldenrod), one collected[3] near New London, Connecticut and the other[4] in Hamilton, Ontario. From ether extracts of the former we have obtained two known diterpenoids, *ent*-16-kauren-19-oic acid (**1**) (2) and (−)-hardwickiic acid (2*a*) (3), and four new diterpenoids which we have named junceic acid (3*a*), junceanol W (4*a*), junceanol X (4*b*), and junceanol Y (5*a*). Of these six compounds all but hardwickiic acid were detected in similar extracts of the Hamilton sample, while in this case an additional new diterpenoid, junceic acid epoxide (6*a*), was isolated. The formulation of these new diterpenoids as shown rests on the evidence which follows.

The ent-Clerodanes

Junceic acid (3*a*) was isolated as an oil by successive column and preparative t.l.c. over silica gel and its molecular formula established as $C_{20}H_{28}O_3$ by mass spectrometry. The acidic nature of the compound was deduced from its behavior on t.l.c. ("streaking"), the broad absorption band between 3000 and 3400 cm^{-1} in its i.r. spectrum and the strong peak at m/e 271 ($M - CO_2H$) in its mass spectrum. The presence of a β-substituted furan moiety in junceic acid, first indicated by its color reaction with Ehrlich's reagent, was readily confirmed by its absorption in the i.r. at 877 cm^{-1} and the three characteristic resonances at τ 2.63, 2.76 (α-furan), and 3.70 (β-furan) in its n.m.r. spectrum. Also clearly evident in the n.m.r. spectra of junceic acid and the derived methyl ester (3*b*), alcohol (3*c*), and acetate (3*d*), m.p. 82–84°, are resonances attributable to an olefinic, a secondary, and a tertiary methyl group, and a vinylic proton. These data were taken to indicate a close structural relationship between junceic and hardwickiic acid and this conclusion was reinforced when the latter (2*a*) was found to be a minor constituent of *S. juncea*.

Two plausible structures, 3*a* and 7*a*, for junceic acid emerged at this point and that one or other did indeed represent the correct constitution and stereochemistry was shown un-

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[1] For Part II see ref. 1.

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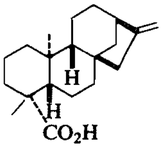
[3] We are indebted to Dr. R. Goodwin, Department of Botany, Connecticut College, for providing this material.

[4] Dr. J. S. Pringle, Royal Botanical Gardens, Hamilton, kindly located this sample.



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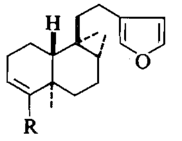
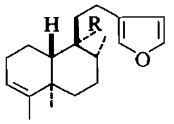


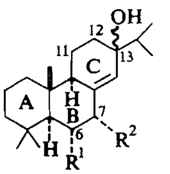
2

a $R = CO_2H$
b $R = CH_2OAC$
c $R = CH_2OH$



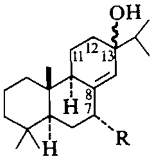
3

a $R = CO_2H$
b $R = CO_2Me$
c $R = CH_2OH$
d $R = CH_2OAc$
e $R = CH_3$
f $R = CHO$
g $R = CH_2OTs$



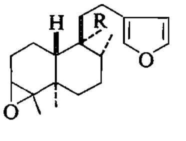
4

a $R^1 = OH; R^2 = OCOC_4H_7$
b $R^1 = OCOC_4H_7; R^2 = OH$
c $R^1 = R^2 = OH$
d $R^1 = R^2 = OAc$
e $R^1 = OH; R^2 = OCOC_4H_9$



5

a $R = OH$
b $R = OAc$

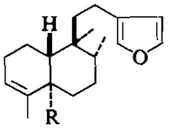


6

a $R = CO_2H$; α-epoxide
b $R = CH_2OAc$; β-epoxide
c $R = CH_2OAc$; α-epoxide
d $R = CO_2Me$; α-epoxide
e $R = CO_2Me$; β-epoxide

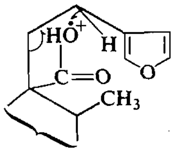
ambiguously by the conversion of both junceic acid and hardwickiic acid (**2***a*) into the furano-olefin (**3***e*). Methyl junceate (**3***b*) on reduction with lithium aluminum hydride formed the alcohol (**3***c*) which was then converted smoothly into the aldehyde (**3***f*) with the Sarett reagent. Huang–Minlon reduction of this aldehyde under carefully controlled conditions yielded the oily furano-olefin (**3***e*), $[\alpha]_D$ −58°. The transformation of hardwickiic acid (**2***a*) into **3***e* was effected via the acetate (**2***b*). This acetate on hydrogenation in triethylamine–ethanol over palladized charcoal suffered hydrogenolysis of the allylic ester group and produced the furano-olefin (**3***e*), identical in all respects with that synthesized from junceic acid.

The decision that **3***a* rather than **7***a* correctly represented junceic acid was made on the following grounds. First, clerodanes with a furan ring in the side chain often (4) have major fragments at M − 95 in their mass spectra resulting from scission of the C_9—C_{11} bond. However, in the case of junceic acid, the ion of this type is absent and replaced by one at *m*/*e* 222 (M − 94), which presumably arises by transfer of a hydrogen atom in a process such as that outlined in **8**. Second, in contrast to solidagoic acid A (**9**) (5), junceic acid does not decarboxylate readily. It was, for example, recovered after heating at 290° under nitrogen for 30 min. Such thermal stability would be surprising for a βγ-unsaturated acid as in **7***a*. Finally, certain n.m.r. data indicate the close proximity of the carboxyl and the secondary methyl group. The magnitudes (see Experimental) of the downfield shifts observed in pyridine for the C—CH_3 resonances on going from the methyl ester (**3***b*) to the acid (**3***a*) reveal (6) not only the 1:3 diaxial arrangement of the carboxyl and the tertiary methyl group but also the juxtaposition of the former to the secondary methyl group. In addition, examination of the spectrum of the alcohol (**3***c*) containing progressively increasing concentrations of tris(dipivalomethanato)europium indicates that the tertiary and the secondary methyl group are similar distances (7) from the interacting europium atom (1.2:1 respectively) while the olefinic methyl and vinylic proton are further removed. This evidence accords only with the structure **3***a* for junceic acid. However, with a view to final confirmation of this, efforts were made to establish the steric relationship between the furan ring and the carboxyl group. To this end, the epoxides **6***b*, m.p. 98–101°, and **6***c* were prepared but attempts to convert the former into the acid (**10**) and thence to the lactone (**11**) failed. An examination of the buffered acetolysis of the toluene-*p*-sulfonate (**3***g*) was next undertaken. No acetates were detected in the product mixture which was shown by t.l.c. on silver nitrate – silica gel to consist essentially of one minor and three major components. These were separated by repeated preparative t.l.c. and tentative structures assigned to the major products on the basis of their u.v. and n.m.r. spectra. As anticipated, all three had retained the β-substituted furan ring and the Δ^3-olefinic bond as evidenced by the characteristic signals for the furanic protons and the C-3 olefinic hydrogen and C-4 methyl group. Surprisingly, they also all contain



7

a $R = CO_2H$
b $R = CH_2OTs$



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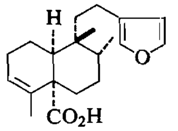

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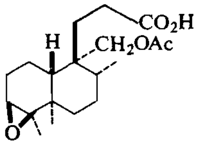

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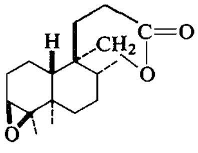

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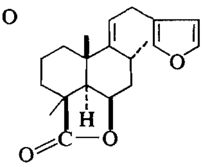

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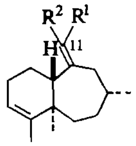
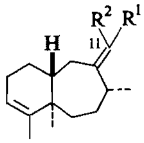


13

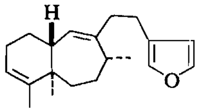
$R^1 = H; R^2 = CH_2Fu$
or
$R^1 = CH_2Fu; R^2 = H$



14

$R^1 = H; R^2 = CH_2Fu$

$R^1 = CH_2Fu; R^2 = H$



15

a secondary methyl group. Further, none of these compounds exhibits absorption in the u.v. arising from conjugation of the newly introduced olefinic bond with either of the unsaturated systems already present. Easily recognized in the n.m.r. spectrum of the compound of intermediate polarity is a new AX_2 system (τ 4.70, 1H, t; 6.89, 2H, d; J = 7 Hz) of the type encountered (8) in anhydromarrubiin (**12**) and attributed to 1 H-11 and 2 H-12. A compound with this functionality would be expected to arise from the toluene-*p*-sulfonate 3*g* rather than from the alternative 7*b* and thus convincingly proves that junceic acid has the constitution and stereochemistry depicted in 3*a*.[5] Bearing in mind its genesis, the furano-diene could be formulated as **13** or **14**. The latter is preferred since double irradiation experiments show that the secondary methyl is coupled (J = 6 Hz) to a proton which resonates as a broad multiplet at τ 7.34, a shift value attributable to an *allylic* proton. The least polar of these solvolysis products also contains the AX_2 system and may be simply the geometric isomer (at C-11) of the compound discussed above. However, in this case, the structures **13** cannot be ruled out since the resonance of the C-8 proton was located by double irradiation at τ 7.67, a value less readily ascribed to an allylic methine. In the third, most polar, furano-diene a new olefinic proton resonates at τ 4.97 (d, J = 6 Hz). Double irradiation experiments showed that this proton and the secondary methyl group are spin–spin coupled to two *different* allylic methines (τ 7.64 and 7.42 respectively) and thus the structure **15** can be assigned to the compound.

The structure of the other new naturally-occurring *ent*-clerodane was readily established as an epoxyjunceic acid (6*a*). Its n.m.r. spectrum is similar to that of junceic acid except that the resonances of the olefinic proton and methyl group are replaced by signals attributable to a proton (τ 7.18) and methyl group (τ 8.90) attached to an epoxide ring. This structural assignment was confirmed by the preparation of the corresponding ester (**6***d*) from methyl junceate. Treatment of the latter (3*b*) with *m*-chloroperbenzoic acid in carbon tetrachloride yielded two epoxides the minor of which (**6***d*) was identical with the methyl ester of the acid

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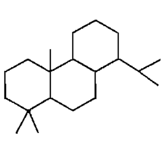
[5] Indeed the compound of structure 7*a*, maingayic acid, has been isolated recently (9) from *Callicarpa maingayi*.

of natural provenance. The C_3—C_4 stereochemistry in these two epoxides can be deduced from the multiplicity of the H-3 resonances. In the major isomer (**6***e*), m.p. 82–86°, H-3 appears as a broadened doublet ($J = 3.5$ Hz) and in the minor (**6***d*) as a singlet. Examination of models and application of a suitably modified (10) Karplus equation leads to the assignments shown. Indeed a preponderance of **6***e* might be expected from the epoxidation reaction since the β-face appears more open to attack.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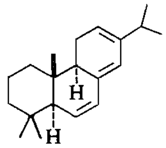

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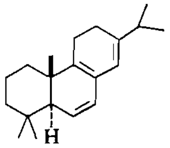

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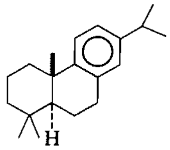

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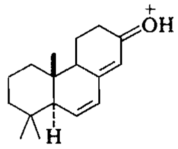

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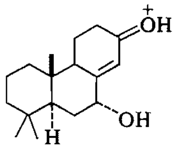

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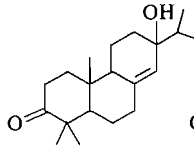

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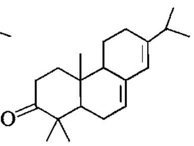

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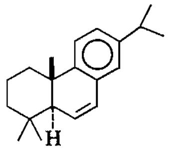

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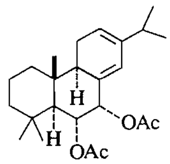

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The Abietanes

Later fractions from column chromatography of the plant extract over silica gel yielded three additional new diterpenoids, junceanols W (**4***a*), X (**4***b*), and Y (**5***a*). The most polar, junceanol Y, m.p. 136–140°, analyzed for $C_{20}H_{34}O_2$. Inspection of the n.m.r. spectrum of the derived monoacetate (**5***b*) reveals the presence of one isopropyl and three tertiary methyl groups as expected for an abietane (or totarane, **16**) skeleton. Only two resonances are present at low field, one attributable to an olefinic proton (τ 4.17). Thus the molecule contains a trisubstituted double bond and a secondary acetate and these together with a tertiary hydroxyl, which gives rise to a peak at about τ 8.3 in its n.m.r. spectrum (lost on D_2O exchange) and at 3615 cm^{-1} in the i.r., account for all the functionality in a tricyclic system.

Definitive evidence for the skeletal structure and the location of the functional groups was next sought. In an attempt to interrelate the tertiary hydroxyl group and the olefinic bond, the monoacetate (**5***b*) was subjected to a variety of conditions, each aimed at its dehydration. However, of these, only one, treatment with toluene-*p*-sulfonyl chloride in pyridine at 100°, proved successful. Separation of the three major products by preparative t.l.c. on silver nitrate – silica gel afforded a stable (**17**) and an unstable (**18**) triene (λ_{max} 315 and 288 nm respectively) and the known (11) abietatriene (**19**), m.p. 38–43°, $[\theta]_{277}$ −320, $[\theta]_{269}$ −320, $[\theta]_{262}$ −120. The production of this last compound allows the assignment of the abietane skeleton to Y and in addition provides unequivocal proof of the absolute configurations at C-5 and -10 (as in **5***a*).

The following arguments suggest that the functional groups are located as shown in **5***a*. The facile formation of the aromatic hydrocarbon (**19**) *and* the nonaromatic trienes (**17** and **18**) from the monoacetate (**5***b*) indicates the probability that two of the functional groups are borne by ring C and the third by ring B. It soon became evident that this indeed is the case. Thus an intense M − 61 peak and an even more intense one for M − 43 in the mass spectrum of Y (**5***a*) were taken as representing the oxonium ions **20** and **21** (or equivalent species) respectively, produced by excision of the isopropyl side chain. This cleavage would be expected (12) for a C-13 tertiary alcohol especially if a $\Delta^{8(14)}$ double bond were also present. This substitution pattern in ring C would also explain the sharpness ($w_{1/2} <$ 3 Hz) of the olefinic proton resonance in Y and its acetate since it would have no vicinal but only long range spin–spin couplings. Confirmation that the olefinic proton and isopropyl group are both in close proximity to the tertiary hydroxyl was obtained by recording the n.m.r. spectrum of the monoacetate (**5***b*) in the presence of tris-(dipivalomethanato)europium. Indeed, the magnitude of the induced shifts (see Experimental) was similar to that obtained for the hydroxyketone (**22**) from *Solidago patula* Muhl. (13) and *S. missouriensis* Nutt. (14). A decision as to the location and orientation of the acetate group in **5***b* was also forthcoming. As mentioned above, the production of the nonaromatic trienes made it appear likely that this third substituent is attached to ring B. Two distinct pieces of evidence allow its assignment to C-7. First, **5***b* is much more stable than the related **22**, which even on standing in chloroform at 20° slowly formed the diene (**23**). This suggests that C-7 is functionalized in **5***b*. Second, although nuclear magnetic double resonance experiments on the monoacetate (**5***b*) failed[6] to show spin–spin coupling between the two protons responsible for the resonances at low field, they did reveal that the proton assignable to *H*COAc is coupled to two protons of near-identical chemical shift, the value of which indicates that they are probably *not allylic*. Irradiation at τ 8.33 (2 H-6) caused the narrow triplet (J = 2 Hz) at 4.73 to collapse to a sharp singlet. A further experiment located the resonance attributable to H-9, since irradiation at τ 7.96 sharpened the singlet at 4.17 (olefinic proton). The multiplicity of the signal at τ 4.73 (see above) indicates the equatorial nature of the proton involved (H-7) and thus the monoacetate of Y can be assigned the structure and stereochemistry shown in **5***b*. The stereochemistry at C-9 is tentatively assigned on a biogenetic basis, while that at C-13 remains unresolved. The structures of junceanols W (**4***a*) and X (**4***b*) discussed below lend credence to the substitution pattern proposed for Y (**5***a*).

The structural similarity of junceanols W and X, first indicated by the observation that they both gave a characteristic pink color when sulfuric acid was used for spot location after analytical t.l.c., was established by the following chemical and spectroscopic studies. The n.m.r. spectra of the two are markedly similar, each containing resonances attributable to an isopropyl and three tertiary methyl groups, an olefinic proton and two protons of the type *H*—C—O. The signals arising from these two protons appeared to suggest that the two compounds are derived from a single diterpenoid which contains two secondary alcohol groups. In W, one of these groups is esterified, while in X, it is the other. Thus the relevant two protons resonate as a doublet (J = 3.5 Hz) and an ill-resolved quartet (J = 3.5, 12 Hz) at τ 4.63 and 6.07 respectively in W and at τ 5.90 and 4.97 respectively in X. The validity of our conclusions as to the relationship of the two compounds was substantiated in two ways. First, distillation of X *in vacuo* furnished a mixture of **24**, X and W, the last resulting from acyl group migration. Second, X and W on saponification or reduction with lithium aluminum hydride produced the same compound (**4***c*). This product on acetylation formed a diacetate (**4***d*) which still showed stretching absorption in the i.r. attributable to a hydroxyl group at 3618 cm^{-1}. This must be tertiary in nature since the n.m.r. spectrum contains no resonances arising from carbinyl protons. It seemed clear that W and X are related to Y but bear an additional oxygen function at C-6. The vicinal nature of the C-6, -7 substituents was demonstrated by a nuclear magnetic double resonance experiment on X. Irradiation at τ 4.97 (H-6) caused collapse of the doublet at τ 5.90 (H-7) to a sharp singlet. The resonance arising from H-5 was located at τ 8.15 since irradiation at this point reduced the quartet at τ 4.97 to a doublet (J = 3.5 Hz). When the n.m.r. spectrum of the diacetate (**4***d*) was run in the presence of a europium shift reagent, H-5 was clearly seen as a clean doublet (J = 12 Hz). The multiplicity of H-6 convincingly demonstrates the equatorial nature of the functional group at C-6. In the thermal conversion of X (**4***b*) into W (**4***a*), described above, the acyl group, although moving from an equatorial to an axial orientation, escapes a strong steric interaction with the geminal methyl groups at C-4. The assignment of the secondary functional groups to ring B rather than ring C, at C-11 and -12, in W and X can be rationalized by arguments analogous to those applied above to Y. However, in addition, it was noted that dehydration of the diacetate (**4***d*) with toluene-*p*-sulfonyl chloride in pyridine afforded, as the major product, the *homocyclic* diene (**25**), λ_{max} 273 nm. Significantly, in the n.m.r. spectrum of this product, neither resonance from the *H*—C—OAc protons had been shifted to appreciably lower field and presumably therefore has not *become* allylic.

Final confirmation of the structure of X as **4***b*, and consequently of W as **4***a*, was achieved by treating it with hydrochloric acid in chloroform. The resulting styrene (**24**) on catalytic hydrogenation furnished the identical abietatriene (**19**) to that prepared earlier from Y. The abso-

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[6] An equatorial proton at C-7 would be expected (15), because of its orientation, to have a minimal coupling to an olefinic proton at C-14.

lute configuration can be assigned with assurance to all centers save C-9 and -13 although the former is tentatively advanced on biogenetic grounds.

Remaining for discussion is the nature of the ester grouping in W and X. An important clue as to its identity was obtained from the n.m.r. spectra of these two compounds which contain three resonances not attributable to the diterpenoid moiety, namely, an olefinic proton at τ 4.31 and two methyl groups attached to an olefinic bond at τ 7.81 and 8.08. This suggested that W and X are senecioates and indeed the corresponding acid was recovered from alkaline hydrolysis of the latter and identified by its n.m.r. and mass spectra.[7]

Experimental

Melting points are uncorrected and were determined on a Kofler hot-stage apparatus. Specific rotations refer to solutions in chloroform unless otherwise stated. For analytical and preparative t.l.c., chromatoplates were spread with Kieselgel G (Merck). G.l.c. was carried out using a Varian Aerograph 1200 gas chromatograph and a stainless steel column ($\frac{1}{8}$ in. × 5 ft packed with 3% SE-30) and nitrogen as carrier gas with a flow rate of 25 ml/min. Light petroleum was of b.p. 60–80°. Microanalyses were by Miss F. Cowan, Glasgow. I.r. solution spectra were recorded in carbon tetrachloride on a Beckmann IR12 or IR5A spectrophotometer, u.v. spectra in ethanol unless otherwise stated on a Unicam S.P.800 spectrophotometer, and circular dichroism curves on a Cary 61 spectropolarimeter. P.m.r. spectra were run on a Varian Associates A-60A or HA 100 spectrometer in carbon tetrachloride, unless otherwise stated, using approximately 0.3 *M* solutions and tetramethylsilane as internal standard. Mass spectra were run on a Varian Associates CH7 instrument.

Isolation Procedure, the Root Extract

(*i*) The ground, dried roots (82 g) of *Solidago juncea* (New London sample) were continuously extracted with ether for 8 h in a Soxhlet apparatus. The extract (4.7 g), which showed one intense and one faint spot on analytical t.l.c. when sprayed with the Ehrlich reagent, was submitted to preparative t.l.c. (ether – light petroleum, 1:4) and four fractions were recovered. Fraction I contained non-polar, essentially non-terpenoid (n.m.r. evidence) material and was not investigated further. Fraction II afforded the major furanoid component, junceic acid (**3***a*, 2.2 g) as an oil, contaminated with a small amount of a second component (n.m.r. evidence), later shown to be *ent*-16-kauren-19-oic acid (**1**). Further purification, by preparative t.l.c. followed by distillation *in vacuo* provided junceic acid (**3***a*) as an oil which had $[\alpha]_D$ −59° (*c*, 0.84); ν_{max} 3400–3000 (br), 1743(w), 1696(s), and 877 cm^{-1} (0.006 *M*); 1743(vw), 1723(s) and 1696(m) cm^{-1} in presence of tetrahydrofuran (0.3 *M*); τ 2.63, 2.76, 3.70 (all m, 1H; furan protons), 4.72 (m, 1 H-3 $w_{1/2}$ = 8 Hz), 8.40 (broad s, 3 H-18), 8.83 (d, 3 H-17, J = 6 Hz), and 9.04 (s, 3 H-19); τ (pyridine) 8.60 (d, 3 H-17, J = 6 Hz) and 8.75 (s, 3 H-19); *m*/*e* 316 (M; $C_{20}H_{28}O_3$). The corresponding methyl ester (**3***b*) prepared by treatment of the acid with diazomethane in ether, was purified by preparative t.l.c. (ethyl acetate – light petroleum, 1:30) and distillation at 160°/0.4 mm. It had $[\alpha]_D$ −54° (*c*, 1.57); ν_{max} 1735 and 878 cm^{-1}; τ 4.83 (m, 1 H-3, $w_{1/2}$ = 7 Hz), 6.47 (s, 3H, —O*CH*$_3$), 8.45 (broad s, 3 H-18; sharpens on irradiation at τ 4.83), 8.88 (d, 3 H-17, J = 6 Hz; s on irradiation at τ 8.34) and 9.20 (s, 3 H-19); τ (pyridine) 8.76 (d, 3 H-17, J = 6 Hz) and 9.06 (s, 3 H-19); *m*/*e* 330 (M).

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.32, H, 9.15. Found: C, 76.58; H, 8.93.

Preparative t.l.c. (acetic acid – ether – light petroleum, 1:2:17) of fraction II (160 mg) afforded the minor component, *ent*-16-kauren-19-oic acid (**1**, 12 mg); **1** was more readily separated as its methyl ester from the mixture resulting from treatment of fraction II with diazomethane. The mixture of esters (250 mg) gave by preparative t.l.c. (ethyl acetate – light petroleum, 1:20; silica gel – silver nitrate, 9:1) the oily methyl ester of **1** (28 mg), which had $[\alpha]_D$ −92° (*c*, 1.55) (lit. (2) $[\alpha]_D$ −104°). Alternatively, reduction of the mixture of esters with lithium aluminum hydride allowed easy separation by preparative t.l.c. (1:15, ethyl acetate – chloroform) of *ent*-16-kauren-19-ol, m.p. 141–143°, $[\alpha]_D$ −85° (*c*, 1.4) (lit. (2) m.p. 143–145°, $[\alpha]_D$ −78°).

Fraction III (190 mg), which contained two furanoid compounds, (t.l.c., Ehrlich stain), was treated with diazomethane. Preparative t.l.c. (ethyl acetate – light petroleum, 1:30, run thrice) afforded in addition to methyl junceate (**3***b*, 28 mg) the more polar (−)-methyl hardwickiate (39 mg), $[\alpha]_D$ −89° (*c*, 1.3) (lit. (3) $[\alpha]_D$ −113.5°), identified by conversion with lithium aluminum hydride into hardwickiol (**2***c*) and comparison (t.l.c., n.m.r.) of this product with an authentic sample (9*b*).

Fraction IV contained polar compounds which were present (t.l.c.) in greater abundance in an extract of the whole plant and are discussed below.

(*ii*) The ground, dried roots (158 g) of *S. juncea* (Hamilton sample) were extracted as above to give an oil (6.3 g). Preparative t.l.c. (acetic acid – ether – light petroleum, 1:2:17) of this oil (1 g) afforded, in addition to junceic acid (**3***a*, 460 mg), epoxyjunceic acid (**6***a*, 18 mg). This compound (**6***a*) was more conveniently separated as its methyl ester. Preparative t.l.c. (ethyl acetate – light petroleum, 1:10, run twice) of the methylated extract (1 g) afforded the oily epoxyester (**6***d*, 47 mg) which distilled at 160°/0.01 mm and had $[\alpha]_D$ −49° (*c*, 2.1); τ 6.43 (s, 3H, —O*CH*$_3$), 7.18 (broad s, 1 H-3), 8.85 (d, 3 H-17, J = 6 Hz), 8.89 (s, 3 H-18) and 9.16 (s, 3 H-19); *m*/*e* 346 (M).

Anal. Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.61; H, 8.85.

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[7] These showed the presence of small amounts of isovaleric acid (less than 10%), thus "compound" X is probably a mixture consisting mainly of **4***a* but in addition a small proportion of the corresponding monoisovalerate (**4***e*). Indeed, a small fraction which was isolated from the original plant extract runs just ahead of **4***a* on t.l.c. and appears on n.m.r., i.r., and mass spectral evidence to consist mainly of **4***e*.

Epoxidation of Methyl Junceate (3b)

Methyl junceate (**3*b***, 166 mg) in carbon tetrachloride (10 ml) was treated with *m*-chloroperbenzoic acid (120 mg) in the dark at 20° for 16 h. The reaction mixture was eluted through a short alumina column with carbon tetrachloride, the solvent evaporated, and the crude product submitted to preparative t.l.c. (ethyl acetate – light petroleum, 1:12, run four times). Three compounds were recovered, unreacted **3*b*** (10 mg), the β-epoxyester (**6*e***, 66 mg), and the α-epoxyester (**6*d***, 20 mg). The less polar epoxyester (**6*e***) after crystallization from light petroleum had m.p. 82–86°; τ 6.44 (s, 3H, —OCH_3), 7.21 (m, 1 H-3, $w_{1/2}$ = 5.5 Hz), 8.87 (s, 3 H-18), 8.88 (d, 3 H-17, J = 6 Hz), and 9.13 (s, 3 H-19).

Anal. Calcd. for $C_{21}H_{30}O_4$; C, 72.80; H, 8.73. Found: C, 73.00; H, 8.78.

The minor, more polar epoxyester (**6*d***) had $[\alpha]_D$ −43° (*c*, 1.0) and was identical (t.l.c., n.m.r., and mass spectral fragmentation pattern) to the methyl ester of the naturally occurring epoxyacid (**6*a***) (see above).

Attempted Decarboxylation of Junceic Acid (3a)

Junceic acid (20 mg) was heated at 290° under nitrogen in a sublimation tube for 30 min and the material was then distilled at the same temperature and 0.2 mm. T.l.c. (ethyl acetate – light petroleum, 1:30 and ethyl acetate – chloroform, 1:15) and its n.m.r. spectrum showed that the distillate was essentially pure starting material.

Reduction of Methyl Junceate (3b) with Lithium Aluminum Hydride

Methyl junceate (**3*b***, 460 mg) was treated with excess lithium aluminum hydride in dry refluxing ether for 20 h. Work-up with saturated aqueous sodium sulfate afforded the crude product (416 mg). Preparative t.l.c. (ethyl acetate – chloroform, 1:15) of this material yielded the oily alcohol (**3*c***, 365 mg) which after distillation *in vacuo* had $[\alpha]_D$ −49° (*c*, 1.3); ν_{max} 3650, 3460, and 877 cm^{-1}; τ 2.72, 2.80, 3.78 (all m, 1 H, furan protons), 4.84 (m, 1 H-3, $w_{1/2}$ = 7 Hz), 6.33 (s, 2 H-20), 8.42 (broad s, 3 H-18), 8.97 (s, 3 H-19) and 9.08 (d, 3 H-17, J = 6 Hz); with a 0.36 M ratio of Eu(DPM)$_3$ to **3*c***, τ −2.2 (m, 2 H-20, $w_{1/2}$ = 9 Hz), 2.35, 2.62, 3.17 (all m, 1H, furan protons), 4.20 (m, 1 H-3, $w_{1/2}$ = 8 Hz), 6.23 (broad s, 3 H-17), 7.15 (s, 3 H-19), 7.87 (narrow m, 3 H-18); m/e 302 (M; $C_{20}H_{30}O_2$).

Treatment of **3*c*** with acetic anhydride – pyridine furnished the corresponding acetate (**3*d***), which was purified by preparative t.l.c. (ethyl acetate – light petroleum, 1:10) and then crystallization from light petroleum. It had m.p. 82–84°, τ 5.92 (s, 2 H-20), 8.04 (s, 3H, —OCOCH_3), 8.43 (narrow m, 3 H-18), 8.98 (s, 3 H-19), and 9.07 (d, 3 H-17, J = 6 Hz).

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.79; H, 9.44.

The Aldehyde 3f

Chromium trioxide (295 mg) in pyridine (10 ml) was added to the alcohol (**3*c***, 150 mg) in the same solvent (10 ml) and the mixture kept at 20° for 6 h. The solvent was removed by azeotroping with benzene and the reaction product (100 mg) recovered from the residue with ether. Preparative t.l.c. (ethyl acetate – light petroleum, 1:20) of the product afforded the unstable aldehyde (**3*f***, 58 mg) as an oil, which had ν_{max} 1715 and 873 cm^{-1}; τ 0.15 (s, 1 H-20), 4.82 (m, 1 H-3), 8.38 (broad s, 3 H-18), 8.92 (d, 3 H-17, J = 6 Hz), and 9.08 (s, 3 H-19); m/e 300 (M; $C_{20}H_{28}O_2$).

The Furano-olefin 3e

The aldehyde (**3*f***, 58 mg) was heated under nitrogen with 99% hydrazine hydrate (2 ml) in ethylene glycol (2 ml) at 85° for 3 days. Potassium hydroxide pellets (145 mg) were then added and the temperature was raised to 195°, allowing excess hydrazine hydrate to distill out of the mixture. After 8 h at this temperature the mixture was allowed to cool and then diluted with ethyl acetate. This ethyl acetate solution was washed successively with dilute sulfuric acid, saturated aqueous sodium bicarbonate, and brine. Preparative t.l.c. (ethyl acetate – light petroleum, 1:20) of the crude product (66 mg) gave the furano-olefin (**3*e***, 37 mg) which had $[\alpha]_D$ −58° (*c*, 1.09); τ 2.73, 2.86, 3.82 (all m, 1H, furan protons), 4.85 (m, 1 H-3), 8.43 (narrow m, 3 H-18), 9.00 (s, 3H, quaternary C—CH_3), 9.14 (d, 3 H-17, J = 6 Hz), and 9.26 (s, 3H, quaternary C—CH$_3$); with a 0.3 M ratio of Eu(DPM)$_3$ to **3*e***, practically no change in spectrum except furan protons, now at τ 2.65, 2.77, and 3.78; m/e 286 (M; $C_{20}H_{30}O$). **3*e*** was identical (n.m.r., mass spectrum, t.l.c., g.l.c. and $[\alpha]_D$) to the furano-olefin obtained (**9*b***) by hydrogenolysis of hardwickiol acetate (**2*b***).

Epoxidation of Acetate 3d

The acetate (**3*d***, 68 mg) was reacted with *m*-chloroperbenzoic acid (45 mg) in carbon tetrachloride for 2.5 h in the dark at 20°. The reaction mixture was washed through a short alumina column with ether and the crude product (53 mg) submitted to preparative t.l.c. (ethyl acetate – light petroleum, 1:10, run twice). Three compounds were isolated, the unreacted acetate (**3*d***, 6 mg) and the epoxyacetates (**6*b***, 32 mg; **6*c***, 11 mg). The less polar β-epoxyacetate (**6*b***) crystallized from light petroleum and had m.p. 98–101°, τ 5.96 (s, 2 H-20), 7.23 (m, 1 H-3, $w_{1/2}$ = 5 Hz), 8.05 (s, 3H, —OCOCH_3), 8.84 (s, 3 H-18), 8.93 (s, 3 H-19) and 9.10 (broadened d, 3 H-17, J = 6 Hz).

Anal. Calcd. for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found: C, 73.23; H, 8.91.

The minor α-epoxyacetate (**6*c***), after distillation *in vacuo*, solidified and had m.p. 85–91°; τ 6.00 (d, 1 H-20, J = 11 Hz), 6.07 (d, 1 H-20, J = 11 Hz), 7.21 (s, 1 H-3, $w_{1/2}$ = 3.5 Hz), 8.03 (s, 3H, —OCOCH_3), 8.88 (s, 3 H-18), 8.97 (s, 3 H-19), and 9.10 (broadened d, 3 H-17, J = 6 Hz).

Anal. Calcd. for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found: C, 73.17; H, 9.16.

Attempted Formation of the Lactone 11

The less polar epoxyacetate (**6*b***, 78 mg) was treated with chromium trioxide (85 mg) in an acetic acid (2 ml) – water (0.2 ml) mixture for 4.5 days. The crude product from work-up, from its t.l.c. behavior (ethyl acetate – light petroleum, 3:2) appeared to be a mixture of acids. Treatment with potassium hydroxide in ethanol (to hydrolyze the acetate) followed by attempted lactonization with toluene-*p*-sulfonic acid in refluxing benzene, or dicyclohexylcarbodiimide in pyridine at 100°, afforded very complex mixtures of mainly polar compounds.

The Tosylate 3g

Toluene-*p*-sulfonyl chloride (470 mg) and alcohol **3*c*** (290 mg) were dissolved separately in pyridine (3 ml each) and the resulting solutions cooled to 0° and then mixed. After 26 h at 20° the reaction was worked-up (ice-water – ether). The resulting tosylate (**3***g*, 445 mg) ran as one spot on t.l.c. (ethyl acetate – light petroleum, 1:6) and had τ 2.27, 2.67 (benzenoid protons), 2.74, 2.90, 3.83 (all m, 1H, furan protons), 4.86 (m, 1 H-3), 5.97 (s, 2 H-20), 7.54 (s, 3H, Ar—CH_3), 8.44 (narrow m, 3 H-18), 9.08 (s, 3 H-19) and 9.12 (d, 3 H-17, J = 6 Hz).

Solvolysis of the Tosylate 3g

A solution of the tosylate (**3***g*, 675 mg) in acetic acid (41 ml) containing sodium acetate (1 g) was heated under reflux for 8 h. The solvent was removed by azeotroping with benzene and the residue dissolved in ether–water. The ether fraction was washed with brine, saturated aqueous sodium bicarbonate, and again brine. Evaporation of the solvent gave an oil (455 mg) which by t.l.c. over silica gel impregnated with silver nitrate (10%) (ethyl acetate – light petroleum, 1:60, or benzene – light petroleum, 1:7) was shown to contain one minor and three major components. Samples of each of the three major constituents were obtained by repeated preparative t.l.c. using the above conditions (ethyl acetate – light petroleum mixture). The least polar furano-diene (**13** or **14**, 50 mg) after distillation at 125°/0.06 mm had $[\alpha]_D$ −126° (c, 1.57); τ 4.75 (m, 1 H-3 and 1 H-11, $w_{1/2}$ = 12 Hz), 6.89 (d, 2 H-12, J = 7 Hz; s on irradiation at τ 4.76), 8.39 (broadened d, 3 H-18, J = 1.5 Hz), 8.94 (d, 3 H-17, J = 6 Hz; s on irradiation at τ 7.67) and 9.12 (s, 3 H-19); *m/e* 284 (M).

Anal. Calcd. for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.25; H, 9.83.

The furano-diene of intermediate polarity (**14**, 37 mg) was distilled at 120°/0.04 mm and had $[\alpha]_D$ −106° (c, 1.8); τ 4.70 (t, 1 H-11, J = 7 Hz; s on irradiation at τ 6.89), 4.83 (m, 1 H-3, $w_{1/2}$ = 8 Hz), 6.89 (d, 2 H-12, J = 7 Hz; s, on irradiation at τ 4.70), 8.41 (broadened d, 3 H-18, J = 1.5 Hz), 9.02 (s, 3 H-19) and 9.04 (d, 3 H-17, J = 6 Hz; s on irradiation at τ 7.34); *m/e* 284 (M).

Anal. Calcd. for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.47; H, 10.03.

The most polar furano-diene (**15**, 67 mg) was distilled at 120°/0.03 mm and had $[\alpha]_D$ −84° (c, 1.12); τ 4.70 (m, 1 H-3, $w_{1/2}$ = 10 Hz; t, J_{obs} = 6 Hz, on irradiation at τ 8.41), 4.97 (d, 1 H-20, J = 6 Hz; s on irradiation at τ 7.64), 8.41 (narrow m, 3 H-18), 8.92 (d, 3 H-17, J = 7 Hz; s on irradiation at τ 7.42) and 9.17 (s, 3 H-19); *m/e* = 284 (M).

Anal. Calcd. for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.45; H, 9.74.

Isolation Procedure, the Whole Plant Extract

Ground, dried, whole plant (120 g) of *S. juncea* was extracted with ether for 9 h in a Soxhlet apparatus. The crude extract (5.2 g) was chromatographed over silica gel (200 g) using light petroleum – ethyl acetate solvent mixtures. Early fractions contained junceic acid. Later fractions (10–40% ethyl acetate) were submitted to repeated preparative t.l.c. (ethyl acetate – light petroleum, 2:1) and afforded (in order of increasing polarity), junceanol W (**4***a*, 120 mg), junceanol X (**4***b*, 950 mg) and junceanol Y (**5***a*, 375 mg). Junceanol W (**4***a*) was obtained as an oil which decomposed fairly rapidly at 20° (t.l.c. evidence). It had ν_{max} 1720 cm^{-1}; τ 4.07 (broad s, 1 H-14, $w_{1/2}$ = 3 Hz), 4.63 (d, 1 H-7, J = 3.5 Hz), 6.07 (q, 1 H-6, J = 3.5, 12 Hz), 8.88, 8.96, 9.20 (all s, quaternary C—CH_3's), 8.92 and 9.06 (both d, 3 H-16 and 3 H-17, J = 6 Hz). Junceanol X (**4***b*), also an oil, on distillation *in vacuo* suffered extensive decomposition (see below). It was purified by further preparative t.l.c. (taking only a central "cut" from the band) and had $[\alpha]_D$ −11° (c, 1.3); ν_{max} (0.0025 M) 3615, 3595 (sh), 3530 (w) cm^{-1}; ν_{max} (0.01 M) 1737, 1720, and 1652 cm^{-1}; τ 4.29 (broad s, 1 H-14 and olefinic proton of senecioate), 4.97 (q, 1 H-6, J = 3.5, 12 Hz; d, J = 3.5 Hz on irradiation at τ 8.15), 5.90 (d, 1 H-7, J = 3.5 Hz; s on irradiation at τ 4.97), 7.35 (broad s, —OH; disappears on D_2O exchange), 7.80, 8.08 (both broad s, senecioate methyls), 8.97 (s, quaternary C—CH_3), 9.07, 9.12 (both d, 3 H-16 and 3 H-17, J = 6 Hz) and 9.13 (s, 6H, quaternary C—CH_3's). Junceanol Y (**5***a*) crystallized from ether – light petroleum and had m.p. 136–140°; $[\alpha]_D$ −34° (c, 2.0); ν_{max} 3600 and 3400 cm^{-1}; τ 4.37 (broad s, 1 H-14, $w_{1/2}$ = 3.5 Hz) 5.7 (broad s, 2 —OH; disappears on D_2O exchange), 5.82 (broad s, 1 H-7, $w_{1/2}$ = 4 Hz), 9.10 (m, 12H, —CH_3's) and 9.28 (s, quaternary C—CH_3); *m/e* 263 (M-43) and 245 (M-61).

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.43; H, 11.11. Found: C, 78.54; H, 11.37.

Hydrolysis of Junceanol X (4b)

Junceanol X (entire t.l.c. band, see above) (**4***b*, 205 mg) was treated with potassium hydroxide (350 mg) in refluxing ethanol (15 ml) for 4 h and the mixture was then diluted with water and extracted with ether. The ether extract was washed with water (the aqueous layer and aqueous washings being retained, see below) and afforded the crude triol (**4***c*, 126 mg). Purification of this material by preparative t.l.c. (ethyl acetate – light petroleum, 2:1) followed by crystallization from moist ether gave **4***c*, m.p. 90–96°; τ 4.30 (broad s, 1 H-14), 5.95 (d, 1 H-7, J = 3.5 Hz), 6.25 (q, 1 H-6, J = 3.5 ,12 Hz), 6.75 (broad s, 2? —OH; lost on D_2O exchange), 8.85, 8.96, 9.25 (all s, quaternary C—CH_3's), 9.06 and 9.11 (both d, 3 H-16 and 3 H-17, J = 6 Hz); *m/e* 304 (M − 18), 280 (M − 42), 279 (M − 43) and 261 (M − 61).

Anal. Calcd. for $C_{20}H_{34}O_3.H_2O$: C, 70.59; H, 10.59. Found: C, 70.32; H, 10.83.

The aqueous fractions from the above reaction were combined, evaporated to near dryness *in vacuo* and acidified with the minimum quantity of dilute sulfuric acid. A large amount of anhydrous sodium sulfate was added and the mixture was then extracted with carbon tetrachloride. The n.m.r. of this solution corresponded to that of a mixture (*ca.* 10:1) of authentic samples of senecioic and isovaleric acids. The above reaction was repeated and the mixture of acids recovered this time in ether. This extract was evaporated carefully to small bulk and submitted to mass spectral analysis which showed *m/e* 100 (senecioic; M) and 60 (isovaleric; M − propene).

Conversions of Junceanol W (4a) into Triol 4c

Junceanol W (**4***a*, 10 mg) was treated with excess lithium aluminum hydride in refluxing dry ether (2 ml) for 1 h. Work-up afforded triol **4***c* (8.5 mg).

Junceanol W (9 mg) was heated in refluxing ethanol with potassium hydroxide (80 mg) for 1 h. The mixture was diluted with ether and then washed with brine. Evaporation of the ether layer gave triol **4***c* (8 mg).

These two samples were identical in n.m.r. and t.l.c. (ethyl acetate – light petroleum, 2:1) behavior to the triol prepared (see above) from junceanol X (**4*b***).

The Acetate 5b

Junceanol Y (**5*a***, 110 mg) was treated with acetic anhydride (0.5 ml) and pyridine (0.5 ml) at 20° for 14 h. The mixture was diluted with ether, washed with saturated aqueous sodium bicarbonate and water, and the solvent evaporated. Preparative t.l.c. (ethyl acetate – light petroleum, 2:1) of the residue afforded the oily acetate **5*b*** (95 mg) which was distilled at 135–140°/0.02 mm and had $[\alpha]_D$ −26° (*c*, 1.3); ν_{max} 3615 and 1735 cm^{-1}; τ 4.17 (broad s, 1 H-14, $w_{1/2}$ = 4 Hz; sharpens on irradiation at τ 7.96), 4.73 (t, 1 H-7, J_{obs} = 2 Hz; s on irradiation at τ 8.33), 8.03 (s, 3H, $—OCOCH_3$), 8.3 (broad s, —O*H*, lost on D_2O exchange), 9.12, 9.17 (both d, 3 H-16 and 3 H-17, *J* = 7 Hz), 9.15 (s, 6H, quaternary $C—CH_3$'s), and 9.24 (s, 3H, quaternary $C—CH_3$); with a 0.46 *M* ratio of $Eu(DPM)_3$ to **5*b***, τ −2.9 (broad s, —O*H*), 0.03 (broad s, 1 H-7), 0.63 (broad s, 1 H-14), 5.32 (s, 3H, $—OCOCH_3$), 7.73 (was 9.12), and 7.91 (was 9.07) (both d, 3 H-16 and 3 H-17, *J* = 7 Hz), 8.25, 8.45, and 8.77 (all s, quaternary $C—CH_3$'s).

Anal. Calcd. for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41. Found: C, 75.59; H, 10.24.

Eu Shifts in Model Compounds

(*i*) Compound **22** (13, 14) had τ 4.53 (broad s, 1 H-14), 8.97 (s, 6H, quaternary $C—CH_3$'s), 9.00 (s, quaternary $C—CH_3$), 9.08 and 9.13 (both d, 3 H-16 and 3 H-17, *J* = 6 Hz); with a 0.42 *M* ratio of $Eu(DPM)_3$ to **22**, τ 1.53 (broad s, 1 H-14), 6.83, 7.21, 7.47 (all s, quaternary $C—CH_3$'s), 7.15 and 7.25 (both d, 3 H-16 and 3 H-17, *J* = 6 Hz).

(*ii*) Compound **23** (13, 14) had τ 4.27 (broad s, 1 H-14), 4.60 (broad s, 1 H-7), 8.91 (s, quaternary $C—CH_3$), 8.98 (s, 6H, quaternary $C—CH_3$'s), and 8.98 (d, 3 H-16 and 3 H-17, *J* = 6 Hz); with a 0.21 *M* ratio of $Eu(DPM)_3$ to **23**, τ 4.16 (broad s, 1 H-14), 4.42 (broad s, 1 H-7), 7.92, 8.12, 8.63 (all s, quaternary $C—CH_3$'s), and 8.93 (d, 3 H-16 and 3 H-17, *J* = 6 Hz).

Treatment of Acetate 5b with Toluene-p-sulfonyl Chloride

The acetate (**5*b***, 165 mg) was heated in pyridine (6 ml) with toluene-*p*-sulfonyl chloride (200 mg) at 100° for 10 h. The reaction mixture was poured into ice-water and extracted with ether. The crude product (124 mg) showed three spots on analytical t.l.c. (ethyl acetate – light petroleum, 1:70) on silica gel impregnated with silver nitrate (10%), and separation of the components was achieved by preparative t.l.c. using the same conditions. The least polar component was the known aromatic hydrocarbon (**19**, 39 mg), m.p. 37–43° (lit. (11) 41–43°); λ_{max} (cyclohexane) 269 (ε 850) and 277 nm (ε 900) (lit. (11) (ethanol) 275 nm (ε 800)); τ 2.93 (d, 1 H-11, *J* = 8 Hz), 3.17 (q, 1 H-12, *J* = 8, 1.5 Hz), 3.23 (broad s, 1 H-14), 8.80 (d, 3 H-16 and 3 H-17, *J* = 6 Hz), 8.83 (s, quaternary $C—CH_3$), and 9.05 (s, 6H, quaternary $C—CH_3$'s); c.d. (ethanol) $[\theta]_{277}$ −320, $[\theta]_{269}$ −320 and $[\theta]_{262}$ −120; g.l.c. retention time 10.9 min at 175°; identical by g.l.c., t.l.c., n.m.r., and c.d. to an authentic sample[8] of **19**. The second component (27 mg) was the oily triene **17** which had λ_{max} 329, 315, and 304 nm; τ 4.13 (m, 1 H-6, 1 H-7, and 1 H-14), 4.38 (broadened t, 1 H-11, J_{obs} = 6 Hz), 8.80, 8.98 (both d, 3 H-16 and 3 H-17, *J* = 6.5 Hz), 8.86 (s, 6H, quaternary $C—CH_3$'s) and 9.15 (s, quaternary $C—CH_3$); *m*/*e* 270 (M). The most polar component (21 mg) was the oily triene **18** which underwent very rapid decomposition (t.l.c.) to more polar material. It had λ_{max} 301 (sh), 288 and 276 nm.

The Diacetate 4d

The triol **4*c*** (126 mg) in pyridine (2 ml) was treated with acetic anhydride (2 ml) at 20° for 15 h. Work-up afforded an oil (156 mg) from which the diacetate **4*d*** (125 mg) was recovered by preparative t.l.c. (ethyl acetate – light petroleum, 1:2). After crystallization from light petroleum **4*d*** had m.p. 114–118°, $[\alpha]_D$ +31° (*c*, 2.7); ν_{max} (0.005 *M*) 3618 (s), 3588 (vw) and 1745 (s) cm^{-1}; τ 4.20 (s, 1 H-14, $w_{1/2}$ = 3 Hz), 4.65 (d, 1 H-7, *J* = 3.5 Hz), 5.02 (q, 1 H-6, *J* = 12, 3.5 Hz), 8.00, 8.09 (both s, 3 H each, $2—OCOCH_3$), 9.00 (s, quaternary $C—CH_3$), 9.06, 9.11 (both d, 3 H-16 and 3 H-17, *J* = 6 Hz) and 9.13 (s, 6H, quaternary $C—CH_3$'s); with a 0.51 *M* ratio of $Eu(DPM)_3$ to **4*d***, τ 0.55 (broad s, 1 H-14), 1.23 (d, 1 H-7, *J* = 3.5 Hz), 3.05 (q, 1 H-6, *J* = 12, 3.5 Hz), 6.73, 7.42 (both s, 3 H each, $2—OCOCH_3$), 6.97 (d, 1 H-5, *J* = 12 Hz), 7.28, 7.43 (both d, 3 H-16 and 3 H-17, *J* = 6 Hz), 8.02, 8.35, and 8.48 (all s, quaternary $C—CH_3$'s).

Anal. Calcd. for $C_{24}H_{38}O_5$: C, 70.90; H, 9.42. Found: C, 70.96; H, 9.66.

Treatment of Junceanol X with Hydrochloric Acid

Concentrated hydrochloric acid (0.1 ml) was added to a solution of junceanol X (**4*b***, 75 mg) in chloroform (1 ml). After *ca.* 2 min, the solution was applied to a preparative t.l.c. plate, heated for *ca.* 1 min with a hair dryer, and the plate then developed with light petroleum in the usual fashion. The major non-polar product was the oily styrene (**24**, 23 mg) which after distillation at 125°/0.1 mm had $[\alpha]_D$ −136° (*c*, 1.55); λ_{max} 266 nm (ε 9000); c.d. (ethanol) $[\theta]_{258}$ +7000; τ 3.06 (d, 2H, aromatic protons, *J* = 1 Hz), 3.21 (narrow m, 1H, aromatic proton), 3.55 (q, 1 H-7, *J* = 10, 3 Hz), 4.07 (q, 1 H-6, *J* = 10, 3 Hz), 7.17 (septet, 1 H-15, *J* = 7 Hz), 7.88 (t, 1 H-5, *J* = 3 Hz), 8.77 (d, 3 H-16 and 3 H-17, *J* = 7 Hz), 8.94, 8.98 and 9.02 (all s, quaternary $C—CH_3$'s); *m*/*e* 268 (M).

Anal. Calcd. for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: C, 89.27; H, 10.68.

Catalytic Hydrogenation of the Styrene 24

The styrene (**24**, 25 mg) in ethyl acetate was shaken with hydrogen over palladized charcoal (5%, 25 mg) for 2 h. Removal of catalyst and solvent left an oil (24 mg) which was purified by preparative t.l.c. (light petroleum) and gave the aromatic hydrocarbon **19** (18 mg). This material was identical (t.l.c., g.l.c., n.m.r., u.v., and c.d.) to the sample of **19** prepared from junceanol Y (see above).

Treatment of Diacetate 4d with Toluene-p-sulfonyl Chloride

The diacetate **4*d*** (80 mg) was heated with toluene-*p*-sulfonyl chloride (95 mg) in refluxing pyridine (3 ml) for 11 h. Work-up afforded an oil (60 mg) which was subjected to preparative t.l.c. (ethyl acetate – light petroleum,

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[8] We cordially thank Professor E. Wenkert for supplying this sample.

1:5), two major constituents being obtained. The less polar component (28 mg) was identified as the styrene **24** by its n.m.r. and t.l.c. behavior. The more polar component (24 mg) was the oily diene **25** which had λ_{max} 273 nm; τ 4.12 (broad s, 1 H-14), 4.45 (d, 1 H-7, J = 3.5 Hz), 4.68 (broad s, 1 H-12), 4.91 (q, 1 H-6, J = 12, 3.5 Hz), 7.97. 8.07 (both s, 3 H each, 2—OCOCH_3), 8.95 (s, quaternary C—CH_3), 9.02 (s, 6H, quaternary C—CH_3's) and 9.07 (d, 3 H-16 and 3 H-17, J = 6 Hz); with a 0.48 M ratio of Eu(DPM)$_3$ to **25**, τ 2.6 (d, 1 H-7, J = 3.5 Hz), 3.73 (broad s, 1 H-14), 3.78 (q, 1 H-6, J = 12, 3.5 Hz), 4.30 (broad s, 1 H-12), 7.13, 7.57 (both s, 3H each, 2—OCOCH_3), 8.63, 8.73, 8.81 (all s, quaternary C—CH_3's) and 9.03 (d, 3 H-16 and 3 H-17, J = 6 Hz).

Distillation–Pyrolysis of Junceanol X

(*i*) Junceanol X (51 mg) was heated at 200° under N_2 for 5 min and the product distilled at that temperature and 0.2 mm. The distillate on t.l.c. (ethyl acetate – light petroleum, 1:2) showed a non-polar compound, one of R_F *ca.* 0.5 and polar material but no substrate. Preparative t.l.c. using the same solvent mixture furnished the two less polar compounds. The first of these was identified as the styrene **24** (12 mg) by its n.m.r. and t.l.c. behavior while the second was identified as essentially pure junceanol W (**4***a*, 18 mg) on similar evidence.

(*ii*) Junceanol X (50 mg) was heated at 270° under nitrogen for 3 min and the product then distilled out at the same temperature and 0.1 mm. The distillate contained no detectable amounts of junceanols W or X (t.l.c. evidence). Preparative t.l.c. (light petroleum) afforded the styrene **24** (6 mg) which was again identified by its n.m.r. and t.l.c. behavior.

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