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PRODUCTS ACTIVE ON ARTHROPOD—5[a]

INSECT JUVENILE HORMONE MIMICS: SESQUITERPENE ACIDS HAVING JH ACTIVITY FROM THE WOOD OF *CEDRUS DEODARA* LOUD[b]

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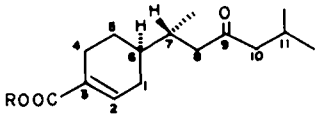
Abstract—Juvenile hormone activity of the wood of *Cedrus deodara* is due to Δ^{10}-dehydroepitodomatuic acid (**6**) and two new related compounds characterised as Δ^{7}-dehydrotodomatuic acid (**8**) and 7-hydroxytodomatuic acid (**13**). Besides these, minor amounts of limonene-8-carboxylic acid, geronic acid, and 4-acetylcyclohex-1-ene-1-carboxylic acid were isolated.

Ever since the discovery of the so-called "paper factor" by Slama and Williams,[1] and its identification[2] as the sesquiterpenoid **1** (juvabione), a constituent of the balsam fir, *Abies balsamea*, the chief source of American paper pulp, there have been several investigations[2b,2c,3-9] on plants in search of juvenile hormone (JH) mimics. Juvabione (**1**) and related compounds have been found to occur in different species of *Abies*[9] and in Douglas fir *Pseudotsuga menziesii* (Mirb.) Franco.[2b,2c] As a matter of fact, todomatuic acid (**2**), the acid corresponding to juvabione, had been known[10] since 1940, as a component of bisulphite-treated pulp oil of *Abies sachalinensis* (Schmidt) and was characterised[11] as **2** in 1963. We now report similar investigations on the wood of *Cedrus deodara* Loud. (Himalayan cedar; in Sanskrit, *devadaaru*).



1 : R = Me
2 R = H

The wood of *Cedrus deodara* Loud. is moderately hard, durable and resistant to attack by termites and therefore, is one of the most valued timbers of India.[12] A report[13] that the acetone extract of the wood exhibits JH activity towards *Dysdercus koenigii* led us to undertake investigation aimed at isolation and characterisation of the JH active compound(s). Both trunk and stump wood, obtained at different times, from different areas, were investigated.

The acetone extract (~18% on the weight of wood) of the debarked wood of *Cedrus deodara* was throughly mixed with Celite and extracted with light petroleum. This extract (60–70% of the acetone extract) showed strong JH activity.[14] Further segregation of this extract into the neutral (85–90%), acidic (7–11%) and "phenolic" parts (1–2%) in the usual manner, showed that only the acid fraction had JH activity. A test portion of the neutral material was found to be almost completely (>95%) steam-volatile and thus essentially corresponds to the total essential oil of the wood, which has already been thoroughly investigated.[15]

Programmed GLC of the derived Me esters of the acid fraction (trunk wood) showed it to be a complex blend of at least twenty constituents, in which three components predominated (accounting for some 45% of the acids). Separation of these compounds proved exceedingly difficult, but finally we were able to isolate two major components via salt formation. The total acids were treated with cyclohexylamine to get a solid salt (m.p. 121–125°) accounting for some 25% of the acid fraction and mostly derived from the three major constituents. After regeneration from the salt, the acids were esterified (CH_2N_2) and further separated by a combination of column chromatography and high performance liquid chromatography (HPLC). This acid composition of the stump wood was equally complex, but quantitatively different in that only one major constituent was present. Separation of this material was carried out by total distillation of methyl esters, followed by their separation by medium-pressure and high pressure chromatography. It may be mentioned that acids from solid cyclohexylamine salts as well as the total distilled Me esters showed high JH activity.

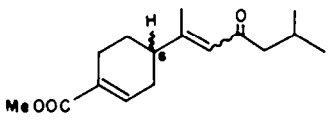
ACIDS FROM CYCLOHEXYLAMINE SALTS (TRUNK WOOD)

Out of the three acids involved in salt formation, only two could be obtained reasonably pure by this method. The one with the least retention time (GLC, RRT = 1), though GLC and TLC pure was clearly a mixture from its PMR spectrum and was not investigated further.

The second compound (RRT = 1.2; $[\alpha]_D$ + 23.4°) analyses for $C_{16}H_{24}O_3$ (M^+, m/z 264) and has the following structural features: HC = COOMe (IR: 1713, 1650, 1252 cm^{-1}. PMR: 3H, s, 3.67 ppm; 1H, bs, 6.91 ppm, W_H = 9 Hz); Me–C=CH–C–C (O) (IR: λ_{max} 237 nm, ϵ = 11040. IR: 1685, 1610 cm^{-1}. PMR: 3H, s, 2.10 ppm; 1H, s, 5.97 ppm); Me–CH–Me (PMR:

[a]Part IV, *Tetrahedron* **40**, 1873 (1984).
[b]M.R.C. Communication No. 46.

6H doublet, 0.91 ppm, J = 7 Hz). These data dictate that the compound is monocarbocyclic and in view of its JH activity, structure **3** appeared attractive. This conclusion is reinforced by the electron-induced fragmentation of the compound, as depicted in **4** and which is in accord with the expected behaviour.[2b,2c,16] Gross structure **3** was confirmed, when it was found that on catalytic hydrogenation (5% Rh-C) it furnished a tetrahydro-derivative (mixture of two isomers), identical (GLC, IR, PMR) with the isomeric mixture obtained by a similar hydrogenation of (+)-Δ^{10}-dehydroepijuvabione (**5**), a compound of known[4,17] absolute stereochemistry, and described below. This correlation also defines the configuration of our compound at C-6, and since its Me–C=CH–C(=O)–C signal occurs at 2.10 ppm (*vide supra*), Δ^7 must have the E-configuration,[16b], leading to stereostructure **7** for our compound, which may now be called (+)-Δ^7-dehydrojuvabione. Since this compound occurs in *Cedrus deodara* as a free acid, following earlier practice,[2,4] the acid is named (+)-Δ^7-dehydrotodomatuic acid (**8**). This is the first report of its isolation from natural source.[18]



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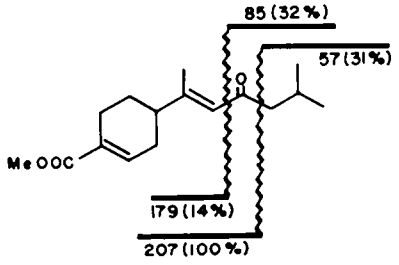

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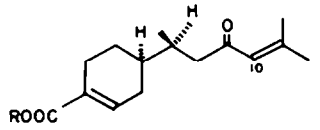
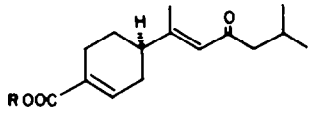


5 : R = Me

6 : R = H



7 : R = Me

8 : R = H

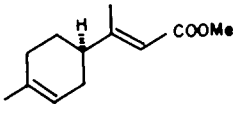
The third compound (RRT = 1.68), $C_{16}H_{24}O_3$ ($\dot{M}^+$, *m/z* 264), from its physical constants ($[\alpha]_D$ + 91.89°. Acid, m.p. 75–78°, $[\alpha]_D$ + 90.42°) and spectral characteristics (Mass, PMR, IR) was readily recognized as the known (+)-Δ^{10}-dehydroepijuvabione (**5**).[4,17] Again, the compound actually occurring in the wood of *Cedrus deodara* is the corresponding acid, (+)-Δ^{10}-dehydroepitodomatuic acid (**6**), which, apparently, has not been so far reported to occur free in nature.

MINOR ACID COMPONENTS (STUMP WOOD)

The total distillable Me esters on medium pressure chromatography, followed by further purification of appropriate fraction(s), led to the isolation of three pure minor components, besides (major) (+)-Δ^7-dehydrojuvabione (**7**) already described earlier.

The three minor constituents, were readily identified from their spectral data (Mass, PMR, IR) as (in order of elution; see Experimental) the known (+)-methyl (E)-limonene-8-carboxylate (**9**),[19] methyl geronate (**10**)[20], and (+)-methyl 4-acetyl-cyclohex-1-ene-1-carboxylate (**11**)[21,22]; Δ^7-dehydrojuvabione (**7**) eluted between compounds **9** and **10**. Compound **11** (or its acid) has not, so far, been reported to occur in nature, and though the synthetic material described in the literature[21,22] has not been resolved, the reason for assignment of absolute stereochemistry in **11**, isolated from *Cedrus deodara*, will become clear from the sequel.

In view of the known propensity of β-hydroxy ketones to dehydration and/or retro-aldol cleavage even under the usual isolation procedures,[23] and the occurrence of Δ^7-dehydrojuvabione (**7**) in *Cedrus deodara* wood, it appeared reasonable to postulate that the C_9-acid (**12**) may be an artefact arising from the hydroxyketo-acid (**13**). This led us to examine the undistilled esters mixture. The mixture was rapidly



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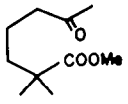

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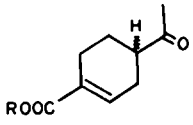
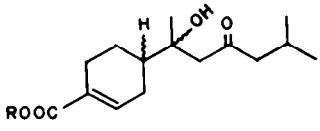


11 : R = Me

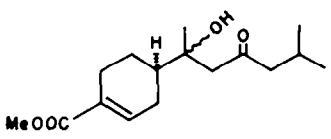
12 : R = H



13 : R = H

14 : R = Me

separated by flash-column-chromatography[23] over a column of mildly active silica gel (grade IV/A), while monitoring the fractions for OH absorption (IR). Further purification of the appropriate cut with preparative-layer-chromatography furnished a liquid product, which from its spectral features (Mass, PMR, IR, UV) was clearly 7-hydroxyjuvabione (**14**): $C_{16}H_{24}O_4$ (M^+, m/z = 282); λ_{max} 221 nm (ϵ, 9815); IR, OH (3500, 1080 cm^{-1}), C=O (1710 cm^{-1}, broad), C=C (1650 cm^{-1}); PMR, Me·CH·Me (6H, d, 0.93 ppm, J = 7 Hz), Me—C—O (3H, s, 1.13 ppm), CH=C-COOMe (3H, s, 3.66 ppm; 1H, bs, 6.90 ppm, W_H = 11 Hz). Confirmation of structure **14** was forthcoming, when exposure of this compound to slightly acidic silica gel (grade II/A) for 2 h resulted in formation of Δ^7-dehydrojuvabione (**7**), in good yield. This transformation also elucidates configuration at C-6, as shown in **15**; stereochemistry of hydroxyl function remains uncertain. Hydroxy-ester **15** on attempted distillation underwent fragmentation (PMR) to the keto ester **11**; part fragmentation also occurred on GLC (5% Carbowax, 150°). In view of these findings, configuration at C-6 in keto ester **11** is as depicted.



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JUVENILE HORMONE ACTIVITY[14]

JH activity of total extract, fractions and pure compounds was tested on 4 hr old last instar nymphs of red cotton bug, *Dysdercus koenigii*, using 10, 1.0 and 0.1 μg of each material in acetone as a topical application and evaluating the results in terms of inhibition of metamorphosis. Farnesyl methyl ether was used as a reference compound. Summary of results is given in Table 1.

EXPERIMENTAL

M.ps are uncorrected and were determined on a Kofler block. Optical rotations were measured in $CHCl_3$ on a Schmidt-Haensch electronic polarimeter (Polartronic—I) or on a Perkin-Elmer spectropolarimeter 141.

The following instruments were used for spectral data: Perkin-Elmer spectrophotometer model 402 (UV); Perkin-Elmer Infracord model 267 (IR); Perkin-Elmer model R32 (90 Mz) NMR spectrometer; Varian Mat CH7 Mass spectrometer (70 eV, direct inlet system). UV measurement were made on EtOH soln. IR spectra were taken on Nujol mulls (solids) or smears (liquids). PMR spectra were measured in ~10% soln in CCl_4 unless otherwise stated; while citing PMR data, following abbreviations have been used: s (singlet), d (doublet), t (triplet), m (multiplet) and b (broad). While summarising mass spectral data, besides the molecular ion, nine most abundant ions (m/z) are reported with their relative intensities.

Silica gel for column chromatography (−100, +200 mesh) was washed with hot water till sulphate-free, dried and activated at 125–130° for 6 hr and standardised.[26] TLC was carried out on silica gel layers (0.3 mm) containing 10% gypsum. Medium-pressure liquid chromatography was done on an Altex column (100.0 × 2.5 cm; packed with Woelm 32–63 grade silica gel) at 40 psi pressure and a flow rate of 10–15 ml/min. HPLC was carried out using a Dupont Liquid Chromatograph848; Zorbax Sil column (25 × 0.46 cm) and Sphero Sil column (44 × 2.5 cm) were used for analytical and preparative separations respectively (254 nm UV detector). GLC was carried out on Aerograph model A-350-8, using 150 cm × 0.6 cm column (A1), packed with 20% diethylene glycol polysuccinate or silicone oil SE-30 on Chromosorb W (60–80 mesh), with H_2 as carrier gas.

Isolation of total acids

Percolation of debarked wood[27] (12.0 kg) which had been coarsely powdered in a hammer mill, with acetone at room temp., yielded after solvent removal (cyclone evaporator; ~200 mm), a thick brownish syrup (1.9–2.2 kg). This (900 g) was thoroughly mixed with Celite (1.8 kg) and the material extracted, by percolation at room temp, with light petroleum (b.p. 60–80°) to furnish, when freed of solvent, a dark brown, pleasant smelling extract (540–630 g). This extract (400 g) was next separated into acids (extraction with 5% Na_2CO_3 aq, 0°; 36.5 g), phenolic (extraction with 2% NaOH aq, 0°; 9.8 g) and neutral (340 g) fractions.

Table 1. Insect juvenile hormone activity

Material	Dose/nymph		
	10	1	0.1 (μg)
	Score*		
Acetone extract	2.2	0.0	-
Acetone→pet. ether extract	1.5	0.0	-
Total crude Me esters	3.4	1.5	0.0
Δ^7-Dehydrojuvibione (7)	3.5	1.5	0.0
Δ^{10}-Dehydrocerojuvabione (5)	3.5	1.5	0.0
7-Hydroxyjuvabione (15)	3.5	1.5	0.0
Farnesyl methyl ether	2.0	0.0	0.0

* Score represents mean of two experiments, each of which was carried out using three replicates of 15 nymphs each. Nymphs which successfully moulted were characterised and scored as under: normal adults (0), adult-nymphs (1), intermediates (2), nymph-adults (3), and sixth instar nymphs (4).

A part of the acid fractions (trunk wood) was esterified (CH_2N_2) and this on programmed GLC (SE-30, 150–270°, 6°/min, 90 ml H_2/min) showed at least 20 components.

Separation of acids via cyclohexylamine salt formation (trunk wood)

A soln of the total crude acids (47.6 g) in dry ether (300 ml) was chilled to −15° and treated with a soln of cyclohexylamine (30 ml) in dry ether (30 ml). Almost immediate precipitation of salt started. The mixture was left in "deep freez" (−15°) for one week, solids collected, washed with chilled (−10°) ether and dried to furnish the salt as a pale yellow amorphous powder, m.p. 121–125°, yield 20.5 g. This salt mixture (14.47 g) was dissolved in CH_2Cl_2 (75 ml) and light petroleum (250 ml), and the soln washed with cold saturated oxalic acid aq (100 ml × 4), water (150 ml × 3) and dried (Na_2SO_4). Solvent removal furnished the acids as a dark brown gum (10 g). This was esterified (CH_2N_2), and dried (Na_2SO_4). Solvent removal furnished the acids as a dark brown gum (10 g). This was esterified (CH_2N_2), and a sample derived from this acid mixture, showed by GLC (diethylene glycol polysuccinate, 195°, 105–110 ml H_2/min) some nine components with RRT of 0.25 (2.3%), 0.36 (0.6%), 0.53 (2.8%), 0.78 (8%), 1.0 (18%), 1.2 (21.4%), 1.42 (3.5%), 1.68 (39.5%), and 2.1 (4%).

The above ester mixture (15 g) was chromatographed on SiO_2 gel (III, 110 cm × 5.1 cm) and eluted with C_6H_6 (250 ml fractions) and after 66th fraction with C_6H_6 containing increasing quantities of MeOH. These fractions were pooled after GLC screening.

(+)-Δ^7-*Dehydrojuvabione* (**7**). Fractions 20–23 (1.05 g) from the above chromatography consisted of compounds with RRT 1 and 1.2. This material was rechromatographed over SiO_2 gel (III, 98 cm × 1.2 cm) and eluted with light petroleum + C_6H_6 (60:40, and then 40:60) and then with C_6H_6 alone, in fractions of 50 ml. Fractions were pooled on the basis of GLC.

Fractions 50–59 (~200 mg) corresponded to compound with RRT = 1, and had the following characteristics: b.p. 160–165° (bath)/0.4 mm, n_D^{30} 1.4851, $[\alpha]_D$ + 62.94 (*c*, 0.9%). Though this fraction was essentially pure by GLC, its PMR spectrum showed it to be a mixture,[28] and it was not studied further.

Fractions 77–78 (~100 mg) corresponded to compound with RRT = 1.2. Though this material was only ~70% pure, and analytically pure sample became available from total distilled esters of stump wood (*vide infra*), and was characterised as Δ^7-dehydrojuvabione (**7**); b.p. 160–165° (bath)/0.6 mm, n_D^{30} 1.4980, $[\alpha]_D^{30}$ + 23.4° (*c*, 1.0%). Mass: *m/z* 264 (M^+, 23%), 232 (24%), 207 (100%), 204 (30%), 147 (35%), 119 (24%), 95 (39%), 85 (32%), 59 (54%), 57 (31%). (Found: C, 72.52; H, 9.11. $C_{16}H_{24}O_3$ requires:C, 72.69; H, 9.15%.)

(+)-Δ^{10}-*Dehydroepijuvabione* (**5**). Fractions 60–64 of the main column chromatography comprised essentially pure **5**: b.p. 185–188° (bath)/0.9 mm, $n_D^{35.5}$ 1.5028, $[\alpha]_D$ + 91.89° (*c*, 3.3%) IR: 1722, 1694, 1652, 1620, 1252, 1082, 1035 cm^{-1}. PMR: Me–CH (3H, d, 0.87 pm, J = 6 Hz), two Me–C=CH (3H singlets at 1.88 and 2.12 ppm), COOMe (3H, s, 3.66 ppm), two C=CH (1H, deformed t, 6.00 ppm; 1H, b signal, 6.90 ppm). Mass: *m/z* 264 (26%), 232 (97%), 204 (55%), 166 (100%), 134 (93%), 125 (82%), 107 (70%), 98 (71%), 83 (81%), 79 (60%). (Found: C, 72.90; H, 9.15. $C_{16}H_{24}O_3$ requires: C, 72.69; H. 9.15%.)

(+)-Δ^{10}-*Dehydroepitodomatuic acid* (**6**). The total crude acid mixture obtained after regeneration from the cyclohexylamine salts, slowly deposited a small quantity of solid, which was repeatedly (8 times) crystallised from CH_3CN at −20° to furnish a solid, m.p. 75–78°, $[\alpha]_D$ + 90.42°. λ_{max} 227 nm (ϵ, 15410). IR: 2600, 1710, 1670, 1645, 1615 cm^{-1}. Its methyl ester (CH_2N_2) was found to be identical (GLC, IR, PMR) with Δ^{10}-dehydroepijuvabione (**5**). Lit[4,17] m.p. 83–85°, $[\alpha]_D$ + 96° for the acid.

Hydrogenation of **7** *and* **5**. Hydrogenation of Δ^7-dehydrojuvabione (**7**) (560 mg) over 5% Rh–C (200 mg) in EtOAc (50 ml), containing 0.5 ml AcOH, at room temp (30°) and pressure (715 mm) furnished, after absorption of H_2 ceased (4 h), tetrahydroderivative (550 mg) as a pale yellow liquid, b.p. 180–182° (bath)/1.5 mm. GLC showed the product to be a mixture of two (?) diastereomers, which were separated by preparative GLC (300 cm × 0.95 cm Al. column, packed with 30% SE-30 on Chromosorb W, 60–80 mesh; 90 ml H_2/min; 290–295°).

Isomer 1: $[\alpha]_D \sim 0°$. λ_{max} 272 nm (ϵ 59). IR: 1730, 1700, 1200, 1150, 1045, 1010, 898, 845, 810 cm^{-1}. PMR: Me–CH (3H, d, 0.81 ppm, J = 6.5 Hz), (Me–CH–Me (6H, d, 0.90 ppm, J = 6.5 Hz), COOMe (3H, s, 3.61 ppm). Mass: *m/z* 268 (M^+, 6%), 211 (57%), 168 (100%), 136 (42%), 127 (78%), 109 (48%), 108 (77%), 85 (50%), 81 (35%), 57 (55%). (Found: C, 71.69; H, 10.43. $C_{16}H_{28}O_3$ equires: C, 71.60; H, 10.52%.)

Isomer 2 (higher RT): $[\alpha]_D \sim 0°$. λ_{max} 272 nm (ϵ 54). IR: 1730, 1700, 1240, 1192, 1170, 1040, 1020, 899 cm^{-1}. PMR: Me–CH (3H, d, 0.81 ppm, J = 6.5 Hz), Me–CH–Me (6H, d, 0.90 ppm, J = 6.5 Hz), COOMe (3H, s, 3.59 ppm). Mass: *m/z* 268 (M^+, 3%), 169 (40%), 168 (100%), 136 (43%), 127 (32%), 109 (53%), 108 (66%), 85 (48%), 81 (31%), 57 (53%). (Found: C, 72.18; H, 10.65. $C_{16}H_{28}O_3$ requires: C, 71.60; H, 10.52%.)

Hydrogenation of Δ^{10}-dehydroepijuvabione (**5**) as above, yielded a product essentially identical (without separation; GLC, IR, PMR) with the mixture obtained from **7**.

Minor acid constituents (stump wood)

The acids from stump wood were esterified (CH_2N_2) and a part (12.0 g) distilled at 100–240° (bath)/0.05 mm to furnish a viscous product (8.0 g), HPLC (pressure, 1000 psi; solvent, MeOH-saturated hexane; flow, 0.6 ml/min; detection, UV 254 nm) of which showed >15 componens, with one predominating.

This material (7.8 g) was subjected to medium-pressure chromatography (40 psi; Altex column, 100.0 × 2.5 cm) using $CHCl_3$ (40 ml × 14) as eluant. First 40 ml × 11 fractions (0.89 g) consisted essentially of fatty acid esters (PMR) and were not investigated further. Next fraction (40 ml) eluted 3.6 g of material, which (2.4 g) was subjected to usual column chromatography (SiO_2-gel IIA; 22 cm × 2.5 cm) using light petroleum and increasing quantities of ether (2 to 20%) as eluant to get the following pure compounds.

(+)-*Methyl* (*E*)-*limonene*-8-*carboxylate* (**9**). After light petroleum (50 ml × 10) and 2% ether in light petroleum (50 ml × 7), 4% ether in light petroleum (50 ml × 6) eluted 98 mg of material, identified from its IR & PMR as 9[19] b.p. 130–135° (bath)/8 mm, n_D^{30} 1.4810. Mass: *m/z* 194 (M^+, 30%), 135 (11%), 101 (40%), 94 (100%), 93 (28%), 87 (19%), 85 (29%), 81 (14%), 68 (14%), 57 (12%).

(+)-Δ^7-*Dehydrojuvabione* (**7**). Next 4% ether in light petroleum fractions (50 ml × 16) furnished a total of 1.1 g of material, which though homogeneous by TLC and GLC, was impure on HPLC. A small quantity of this was purified by preparative HPLC (solvent, MeOH-saturated hexane; flow, 60 ml/min; presure, 1000 psi) to get pure **7** (*vide supra*).

Methyl geronate (**10**). The material next eluted (0.2 g; 4% ether in light petroleum, 50 ml × 4) was a mixture, but the following fractions (8% ether in light petroleum; 50 ml × 8) eluted a fairly pure product (100 mg), further purified by preparative GLC, and identified (IR, PMR) as the known methyl geronate (**10**).[20]

(+)-*Methyl* 4-*acetylcyclohex*-1-*ene*-1-*carboxylate* (**11**). Next eluates (10% ether in light petroleum, 50 ml × 8) furnished 62 mg of an ester, which was 92% pure by GLC: b.p. 145–150° (bath)/5 mm, n_D^{30} 1.4913, $[\alpha]_D$ + 3.8° (*c*, 3%). λ_{max} 220 nm (ϵ, 6100). IR: 1725, 1705, 1650, 1260, 1170, 1090, 1045 cm^{-1}. PMR: MeCO·C (3H, s, 2.13 ppm), COOMe (3H, s, 3.68 ppm), C=CH (1H, b signal, 6.93 ppm). Mass: *m/z* 182 (M^+, 11%), 150 (40%), 139 (74%), 108 (11%), 107 (50%), 80 (10%), 79 (50%), 77 (25%), 59 (17%), 43 (100%).

7-Hydroxyjuvabione (**15**). The Na_2CO_3 extract, (3 l; from 327 g of light petroleum extract) as described under "isolation of total acids" and obtained from stump wood was cooled to 0° and acidified with 5% H_3PO_4 aq at ~0° (acidic to litmus) and extracted with ether (500 ml × 6) at ~0°, the extract washed with water and dried. The extract was freed of solvent at room temp to get 29 g of crude acids. A part material (1.5 g) was esterified (CH_2N_2) and the ester mixture flash-chromatographed on SiO_2-gel (IVA, 30 cm × 1.5 cm), using light petroleum and light petroleum containing increasing quantities (2-20%) of ether and eluants, while monitoring the eluted material for OH bonds (IR). 20% Ether in light petroleum (40 ml × 2) eluted 97 mg of an ester showing strong OH absorptions. This material was further purified by preparative TLC (solvent: 1:1 ether-light petroleum) to afford pure **15** (32 mg) as a gum,[29] n_D^{30} 1.4942. Mass: *m/z* 282 (M⁺, 2%), 264 (11%), 180 (13%), 179 (12%), 164 (17%), 143 (54%), 140 (54%), 105 (12%), 85 (100%), 57 (50%).

Adsorptions of this material (26 mg), in light petroleum, on SiO_2-gel (IIA, pH, 4; 2.0 g), and elution after 2 h, yielded 18 mg of a product, identified (TLC, GLC, IR, PMR) as Δ^7-dehydrojuvabione (**7**).

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[17]Dehydrojuvabione described by Cerny *et al.*[4] is, in fact, dehydroepijuvabione, as shown by Manville,[9b] who also clarified its absolute stereochemistry.

[18]Presence of Δ^7-dehydrojuvabione in the wood of *Abies lasiocarpa* (L.) Mill. was tentatively *inferred* by Manville and Kriz[9f] from PMR spectra of certain impure chromatographic fractions of the wood extract.

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[27]Trunk wood was procured from Haldwani, U. P., while the stump (ten-year old) wood came from Hardwara, Keshmir.

[28]The spectral data (IR, PMR & Mass) was consistent with the major component being (+)-juvabione[9f]/(+)-epijuvabione[4,9b]

[29]Since this product could not be distilled without decomposition, an acceptable analysis (C, H) could not be obtained.