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DITERPENES OF *CALOCEDRUS DECURRENS*

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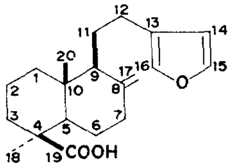
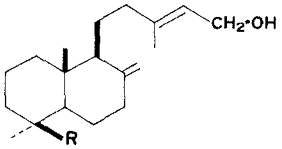
Key Word Index—*Calocedrus decurrens*; Cupressaceae; oleoresins; lambertianic acid; pinusolide; labdane diterpenes

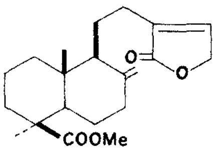
Plant. Calocedrus decurrens (Torrey) Florin (*Libocedrus decurrens* Torrey Incense cedar). *Source* Near State Highway 4 above Murphys, Calaveras Co., California *Previous work.* Heartwood extracts[1] Leaf biflavonyls,[2] alkanes,[3] lipids[4]



(1)



(2) R = COOMe
(3) R = CHO



(4)

Exuded trunk resin. GLC of the methylated resin showed four major components and many minor ones Three of the major peaks corresponded to the esters of sandaracopimaric, dehydroabietic, and lambertianic (**1**) acids while the fourth, emerging much later, was unknown The identity of the aforementioned compounds was confirmed by their isolation together with a further component, methyl isocupressate (**2**),[5] by column chromatography of the acid fraction The unknown component, a methyl ester lactone, was isolated from the methylated acid fraction and also, more readily, from the neutral fraction, which also yielded the aldehyde isoagatholal (**3**)[6,7] Despite a discrepancy in the optical rotations the ester lactone is clearly identical with pinusolide (**4**),[8] previously isolated from the resins of *Pinus koraensis* and *P sibirica*, where it also occurs with lambertianic acid. The finding of the latter here is the first outside the Pinaceae The absence of diterpene phenols and presence of dehydroabietic acid without abietadiene acids is also noteworthy

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TABLE 1 DITERPENES OF *Calocedrus decurrens* RESIN

RR_t at 193° XE-60	OV-1	Component	Approximate % of resin
1	1	Sandaracopimaric acid	8 5
1 06	1	*Trans*-communic acid	2
1 4	1 26	Dehydroabietic acid	17
1 53	1 26	Lambertianic acid	13
3 72	2 06	Isocupressic acid	4
4 3	1 82	Isoagatholal	1
5 4	2·58	7-Oxo-dehydroabietic acid	2
17 8	4 4	Pinusolide	6 5

The percentages were determined on a bulked sample of resin from several trees using an internal standard RR_t s refer to methyl esters where appropriate The percentage for pinusolide includes that present as the free acid, about half of it The resin sample was several years old and the percentage of *trans*-communic acid is higher, that of 7-oxo-dehydroabietic acid lower, in fresh material These two compounds were not confirmed by isolation Seven individual resin samples from wild and cultivated trees showed qualitatively similar results but fairly wide quantitative variation

EXPERIMENTAL

Rotations are in $CHCl_3$, NMR spectra in $CDCl_3$ at 100 MHz The resin (100 g) in Et_2O was divided into neutral (15 g) and NaOH aq-soluble acid fractions Chromatography of the neutral fraction on SiO_2 and elution with 5% Et_2O–C_6H_6 gave pinusolide (2 4 g) m p 81–83° (from hexane) $[\alpha]_D + 64°$ (*c*, 1 1) (Reported[8] m p. 82–83°, $[\alpha]_D + 25°$, *c*, 0 05) NMR identical to that reported While the compound showed a positive Raymond test[9] and a positive Legal test under the controlled conditions of Elderfield *et al* [10] ($\alpha\beta$-butenolide), its IR spectrum showed an unsplit lactone absorption at 1766 (CCl_4) or 1754 cm^{-1} ($CHCl_3$) (no α-H) (Found C, 72 84, H, 8 67 Calc for $C_{21}H_{30}O_4$ C, 72 8, H, 8 73%) MW 346 (MS) Further elution with 6–10% Et_2O–C_6H_6 gave an oil which after further purification by PLC proved to be isoagatholal (**3**) labda-8(17),13-diene-15-ol-19-al) NMR, δ 0 56 (3H, C-20), 1 01 (3H, C-18), 1 65 (3H, C-16), 4 12 (*d*, *J* 7 Hz, 2H, C-15), 4 54 and 4 86 (2H, C-17), 5 36 (*t*, 1H, C-14), and 9 71 (1H, C-19) The acid fraction in Et_2O was divided into acids forming, and acids not forming, insoluble cyclohexylamine salts in the usual way Chromatography of the acids not forming cyclohexylamine salts on SiO_2 and elution with CH_2Cl_2 gave lambertianic acid (**1**)[11] m p 125–127° (from hexane), raised to 155–159° on admixture with its enantiomer daniellic acid[12] (illurinic acid[13]) $[\alpha]_D + 59°$ (*c*, 1 7) NMR and IR as reported MW 316 (MS) Further elution with 5% Me_2CO–CH_2Cl_2 gave an oily lactone acid (IR) which after methylation (CH_2N_2) and further purification by PLC gave pinusolide m p 80–82°, identical to that obtained from the neutral fraction Further elution with 10 and 20% acetone–CH_2Cl_2 gave a hydroxy-acid fraction which after methylation and PLC afforded methyl isocupressate (**2**)[5] as an oil $[\alpha]_D + 48°$ (*c*, 2 1) IR as reported, NMR marginally different, δ 0·51 (3H, C-20), 1 22 (3H, C-18), 1 67 (3H, C-16), 3 62 (ester Me), 4 13 (*d*, *J* 7 Hz, 2H, C-15), 4 52 and 4 84 (2H, C-17), 5 38 (*t*, 1H, C-14) MW 332 (MS) Chromatography of the acids forming cyclohexylamine salts on SiO_2 gave a fraction containing predominantly C-18 (equatorial) acids Methylated and chromatographed on $AgNO_3$–SiO_2 this yielded methyl dehydroabietate m.p and mixed m p 62–64°, $[\alpha]_D + 57°$ (*c*, 1 7), and methyl sandaracopimarate m p and mixed m p 64–68°, $[\alpha]_D - 18°$ *c*, 1 9)

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