Chromatography of the 179 mg of combined material on 18 g of 40% $AgNO_3$–alumina in a 1·2 cm i.d. column with petroleum ether–benzene (10:1) yielded 97 mg of isopimarate-free product. Further purification by GPC followed by preparative GLC on 5% OV-225 yielded 42 mg of a colorless oil that showed no impurities on GLC or $AgNO_3$–alumina–TLC. The compound was distilled at a pot temperature of 143° (0·05 mm). (C, 79·15; H, 10·93 Calc. for $C_{21}H_{34}O_2$: C, 79·19; H, 10·76%); $[\alpha]_D^{22}$ + 46° (c 0·5, $CHCl_3$) (lit.[4] for methyl copalate, $[\alpha]_D$ -45°); η_D^{21} 1·5152 (lit.[5] η_D^{20} 1·5130); $\lambda_{max}^{isooctane}$ 217·9 (ϵ = 15700) and 200·6 nm (ϵ = 17000) (conditions, see Burgstahler *et al.*[18]; ν_{max}^{film} 3041, 1650, 890 (olefin) and 1727, 1228, 1151 cm^{-1} (ester); NMR ($CDCl_3$), τ 4·33 (quartet, J = 1, one olefinic H), 5·15 and 5·49 (singlets, $=CH_2$), 7·33 (sharp singlet, Me ester), 7·86 (doublet, J = 1, CH_3C = C, *cis* to ester), and 9·13, 9·20, and 9·32 (sharp singlets, 3 tertiary Me); *m/e* 318 (98%, M^+), 303 (100%, M^+-CH_3), 287 (12%, M^+-CH_3OH), 244 (35%, M^+-CH_3COOCH_3), 205 (71%, $C_{15}H_{25}^+$), 204 (60%, $C_{15}H_{24}^+$), 137 (78%, $C_{10}H_{17}^+$), 114 (80%, $C_6H_{10}O_2^+$), 95 (100%, $C_7H_{11}^+$), and 81 (99%, $C_6H_9^+$). Cf. reported spectra.[2,4,5] Anticopalic acid was isolated as the methyl ester (CH_2N_2) in a similar manner from western white pine wood (sample from the Clearwater National Forest in Idaho).

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[18] A. W. BURGSTAHLER, J. N. MARX and D. F. ZINKEL, *J. Org. Chem.* **34**, 1550 (1969).

Phytochemistry, 1971, Vol. 10, pp. 1163 to 1164. Pergamon Press. Printed in England.

ANGIOSPERMAE

APOCYNACEAE

CONSTITUENTS OF *ANODENDRON AFFINE*

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Plant. Anodendron affine (Hook. et Arn.) Durce.

Previous work. Alkaloid[1] and flavonoid.[2]

Stems. The MeOH extract concentrated, diluted with H_2O and filtrated. The filtrate fractionated with Et_2O and $CHCl_3$. The aqueous layer concentrated to dryness and extracted with $CHCl_3$–MeOH (2:1) by heating at 100°. The precipitate extracted with benzene and separated into acidic and neutral fractions with aq. alkali.

β-Sitosterol $C_{29}H_{50}O$ (m.p., mixed m.p., i.r. and TLC of alcohol and acetate): from neutral fraction, chromatographed on silica gel.

[1] K. SASAKI and Y. HIRATA, *Tetrahedron Letters* 4065 (1969).
[2] I. INAGAKI, S. HISADA, S. NISHIBE and K. SHIMA, *Abstracts of Papers, Meeting of Tokai Branch*, p. 17, Pharmaceutical Society of Japan, Gifu (1969).

β-Sitosterol-*O*-glucoside $C_{35}H_{60}O_6$ (m.p., mixed m.p., i.r. and TLC of glucoside and acetate): from precipitate by aq. alkali, chromatographed on activated charcoal. Acid hydrolysis to β-sitosterol and glucose.

New cardenolide m.p. 225–227° (decomp.): from $CHCl_3$ fraction, chromatographed on silica gel. (Found: C, 62·95; H, 6·83. $C_{30}H_{38}O_{11}$ required: C, 62·72; H, 6·62%.) Mass spectrum M^+ 574. I.r. ν_{max} ($CHCl_3$), 1790, 1760, 1630 cm^{-1} (α,β-unsaturated γ-lactone), 1710 cm^{-1} (carbonyl), u.v. λ_{max} (EtOH), 213, 285 mμ. Further study is in progress.

Sucrose $C_{12}H_{22}O_{11}$ (m.p., mixed m.p., i.r. and TLC of sugar and acetate): from $CHCl_3$–MeOH (2:1) fraction, chromatographed on activated charcoal, eluted by H_2O. Acid hydrolysis to fructose and glucose. Dambonitol $C_8H_{16}O_6$ (m.p., mixed m.p., i.r. and TLC of cyclitol and acetate): from the same fraction as sucrose, eluted by H_2O–MeOH (99:1).

Flowers. Extracted and fractionated as for stems.

Ursolic acid $C_{30}H_{48}O_3$ (m.p., mixed m.p., i.r. and TLC of alcohol and acetate) from precipitate.

COMPOSITAE

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KAURANOID DITERPENES IN *ESPELETIA GRANDIFLORA*

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Abstract—The resin of *Espeletia grandiflora* contains (−)-kaur-16-en-19-ol, (−)-kaur-16-en-19-al (not previously isolated from natural sources), (−)-kaur-16-ene and (−)-kaur-16-en-19-oic acid.

FROM the neutral extract of the resin of *Espeletia grandiflora* Humb. et Bonpl. (Compositae) we have isolated some diterpenoids, whose identification we wish to report.

A first product, white needles m.p. 114° (from EtOH), $[\alpha]_D^{20°} = -95°$ (EtOH; c, 0·39), gives positive tetranitromethane and dinitrophenylhydrazine tests, and has $C_{20}H_{30}O$ formula. Mass spectrum: 286 (M^+), 271 (M–15), 258 (M–28), 257 (M–29). I.r. spectrum (nujol mull): 2715 and 1718 cm^{-1} (CHO), 1658 and 880 cm^{-1} (C=CH_2). NMR spectrum (100 MHz, CCl_4): 0·89 δ (S, *t*-Me), 0·97 δ (S, *t*-Me), 2·03 δ (T, J=1 Hz, 2H), 2·59 δ (broad, 1H), 4·68 and 4·73 δ (C=CH_2), 9·64 δ (D, $^4\sigma J$=1·2 Hz, CHO).

Such evidence is indicative of a tetracyclic kauren-like structure with an axial aldehyde group on C-4, as proved by the mass spectrum fragmentation and by the characteristic