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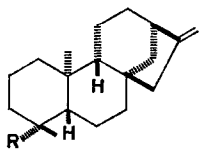
Abstract—The resin of *Espeletia grandiflora* contains (−)-kaur-16-en-19-ol, (−)-kaur-16-en-19-al (not previously isolated from natural sources), (−)-kaur-16-ene and (−)-kaur-16-en-19-oic acid.

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

doublet at 9·64 δ in the NMR spectrum[1–5]: the triplet at 2·03 δ must be attributed to the two protons on C-15 and the signal at 2·59 δ to the allylic proton on C-13. The above results are hence consistent with the structure (I) of (−)-kaur-16-en-19-al; $LiAlH_4$ reduction of (I) to the known (−)-kaur-16-en-19-ol (II) and Huang–Minlon transformation of (I) into (−)-kaur-16-ene (III) confirm this attribution; careful Jones oxidation of (II) gives (I) again. The identification of (II) and (III) is supported by comparison with authentic specimens.



(I) R = CHO
(II) R = CH_2OH
(III) R = CH_3
(IV) R = COOH

A second product, m.p. 140–141° (from cyclohexane), $[\alpha]_D^{20°} = -82°$ (EtOH; c, 0·42), gives positive tetranitromethane test, and has $C_{20}H_{32}O$ formula. Mass spectrum: 288 (M^+), 273 (M–15), 257 (M–31). I.r. spectrum: 3350 cm^{-1} (OH), 1655 and 880 cm^{-1} (C=CH_2). NMR spectrum (60 MHz, $CDCl_3$): 0·95 δ (S, *t*-Me), 1·02 δ (S, *t*-Me), 2·66 δ (broad, allylic H-13), 3·45 and 3·77 δ (Q_{AB}, J=11 Hz, axial CH_2OH on C-4), 4·80 δ (broad, C=CH_2). The data here reported are in full agreement with those known for (−)-kaur-16-en-19-ol (II); the identity is confirmed by comparison with an authentic specimen.

As a recent investigation by Brieskorn[6] on the akin species *Espeletia schultzii* Wedd. had resulted in the isolation of (−)-kaur-16-ene (III), we have then accomplished a search for this hydrocarbon in the less polar fraction of the neutral extract of the resin from *Espeletia grandiflora*: actually, we have succeeded in detecting small amounts of (III) by GLC on different columns (cross injections with sure sample of the hydrocarbon).

Kaurenal (I) and kaurenol (II) had never been previously obtained as natural products: kaurenol had been prepared by $LiAlH_4$ reduction[4] of (−)-kaur-16-en-19-oic-acid (IV), a natural occurring diterpene acid. Occurrence of (I) and (II) as intermediates in the biogenetic conversion of kaurene into kaurenoic acid had been reported:[7,8] however, both products had been detected by tracer chromatography methods in the endosperm homogenate of *Echinocystis macrocarpa* Greene. The present isolation of substantial amounts allows to regard (I) and (II) as real natural products.

In the acidic extract of the resin, near grandiflorolic acid[9] and grandiflorenic acid,[10] we have found minor amounts of (−)-kaur-16-en-19-oic acid, (IV) isolated as its methyl

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ester by chromatography on silica gel-$AgNO_3$ or by preparative GLC: m.p. 81° (mixed m.p. with pure specimen), MS 316 (M^+), identical T_R on GLC (crossed injection with an authentic sample).*

The co-occurrence of kaurene, kaurenol, kaurenal and kaurenoic acid in the same plant is novel and supports the theory involving biogenetic transformation of kaurene into kaurenoic acid and then into gibberellic acid.

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MELIACEAE

THE ISOLATION OF ANGUSTINOLIDE FROM *GUAREA TRICHILIOIDES* L.

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Abstract—The occurrence of the tetranortriterpenoid, angustinolide, in the seeds of *Guarea trichilioides* L. as well as minor amounts of β-sitosterol in the bark and wood extracts are recorded.

Plant. Guarea trichilioides L.—*Meliaceae.*

Occurrence. Tropical regions; found in Rio de Janeiro, Minas Gerais, Matto Grosso, Brazil.

Source. Jardim Botánico de Rio de Janeiro, Rio de Janeiro, Brazil.

Uses. Medicinal, helminticide.[1]

Previous work. Toxic principle in the fruits,[2] on sister species.[3-6]

Seeds. (900 g) The light petrol and $CHCl_3$ extracts (102 g) were chromatographed on silica columns. The benzene–$CHCl_3$ 1:1 and the $CHCl_3$ eluates gave 1·4 g of angustinolide[7] (0·15%), m.p. 168–170° (MeOH), mixed m.p., co-chromatography and i.r. spectra with an authentic sample.

Bark. (2·5 kg) The petrol extract furnished an oily residue (12 g, 0·48%). The then defatted material was treated with MeOH under reflux and the extract (8·6 g) chromatographed (SiO_2): β-sitosterol (0·006%) from the benzene eluates. Elutions with $CHCl_3$ and MeOH afforded low yields of complex mixtures which proved difficult to resolve.

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