

Fruit pulp. EtOH concentrate, extrn. ethyl acetate; *n*-hexane soluble fraction: *Hexacosane*, $C_{26}H_{54}$, m.p. mixed¹⁰ m.p., ν_{\max}^{KBr} 722 cm^{-1} (alkane chain),¹¹ superposable. *Hexacosanol*, $C_{26}H_{54}O$, m.p., mixed¹⁰ m.p., i.r.; acetate, $C_{28}H_{56}O_2$, m.p., i.r. β -*Sitosterol*, m.p., $[\alpha]_D$, mixed m.p., i.r., co-TLC, benzoate, m.p., i.r.

New compound. Monohydroxy triterpene ketone, m.p. 196–197°, $[\alpha]_D^{35} + 60^\circ$, TLC single spot, LB and TNM positive, ν_{\max}^{KBr} 3500(OH), 1700(CO) cm^{-1} , mol. wt. 440 (M^+), found: C, 82.00; H, 11.18. $C_{30}H_{48}O_2$ required: C, 81.81; H, 10.91%.

Betulin. $C_{30}H_{50}O_2$, m.p., $[\alpha]_D$, mixed³ m.p., i.r., co-TLC, diacetate, $C_{34}H_{54}O_4$, m.p., $[\alpha]_D$, i.r. *Lupeol*, $C_{30}H_{50}O$, m.p., mixed¹² m.p., $[\alpha]_D$, i.r., co-TLC; m.p., $(\alpha)_D$, i.r. of acetate and benzoate.

n-Hexane insoluble fraction: β -*D-Glucoside of β -sitosterol*, $C_{35}H_{60}O_6$, m.p., mixed¹² m.p., $[\alpha]_D$, co-TLC, i.r.; m.p., $[\alpha]_D$ of tetraacetate, $C_{43}H_{68}O_{10}$ and tetra-benzoate, $C_{63}H_{76}O_{10}$; acid hydrolysis to glucose and β -sitosterol.

Ethyl acetate soluble, conc. and crystn. (water): *Gallic acid*, m.p., mixed m.p., co-TLC (spray, $FeCl_3$ – $K_3Fe(CN)_6$),¹³ i.r.

Seed. Stony hard; extrn. EtOH, *n*-hexane soluble fraction: *Betulinic acid*, $C_{30}H_{48}O_3$, m.p., mixed¹⁴ m.p., $[\alpha]_D$, co-TLC, i.r.; m.p., mixed¹⁴ m.p., $[\alpha]_D$, i.r. of methyl ester, $C_{31}H_{50}O_3$ and methyl ester acetate, $C_{33}H_{52}O_4$.

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LEGUMINOSAE

TERPENOIDS FROM *COPAIFERA LANGSDORFII*

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Abstract—The oleoresin of *Copaifera langsdorfii* L. has been found to contain some sesquiterpene hydrocarbons and diterpene acids. Caryophyllene, copaene, β -bisabolene, polyalthic acid, (–)-kaur-16-en-19-oic acid, (–)-16 β -kauran-19-oic acid and eperu-8(20)-en-15,18-dioic acid were isolated.

Plant. Copaifera langsdorfii L.

Occurrence. Brazil.

Previous works. Wood,¹ seeds.²

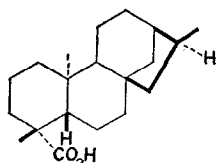
The oleoresin from *Copaifera langsdorfii* L. contains about 50% of isomeric sesquiterpenic hydrocarbons $C_{15}H_{24}$ (MS-GLC) and 25% of diterpenic acids with (–)-labdanic and (–)-kauranic skeletons.

The hydrocarbon fraction, isolated by column chromatography, on examination by GLC and TLC (silica gel-silver nitrate) appears to contain at least 8 substances. The 3 main compounds were isolated by preparative GLC and identified as caryophyllene, copaene and β -bisabolene by direct comparison of GLC and i.r. spectra with authentic samples.³ The less abundant hydrocarbons have the same retention-time in GLC of α -bourbounene, cyperene, humulene and γ -cadinene.³

The main constituent of the acidic fraction is polyalthic acid^{4,5} [methyl ester: $[\alpha]_D^{20} -34^\circ$ ($CHCl_3$); λ_{max} (MeOH): 210 nm (ϵ 9800); MS⁶: m/e 330 M^+ , 121 (100%), 81 (75%); cyclohexylamine salt: m.p. 190–5°; $[\alpha]_D^{20}$ ($CHCl_3$)].

Among the constituents of the acidic fraction (–)-kaur-16-en-19-oic acid^{5,7} [methyl ester: $[\alpha]_D^{20} -102^\circ$ ($CHCl_3$); MS: m/e 316 M^+ , 94 (100%)] and (–)-16 β -kauran-19-oic acid (I) [m.p. 205–11°; $[\alpha]_D^{20} -70^\circ$ ($CHCl_3$); NMR ($CDCl_3$): 0.96 δ (3 H, s), 1.04 δ (3 H, d, $J=6$ Hz), 1.24 δ (3 H, s); MS (on methyl ester): m/e 318 M^+ , 123 (100%), 259 (86%)] were isolated.

The acid (I) was never found in nature, but only obtained from (–)-kaur-16-en-19-oic acid by hydrogenation⁵ or from hydroxykaurenolide.⁸



(I)

The most polar compound of the acidic fraction is the eperu-8(20)-en-15,18-dioic acid⁹ [m.p. 144°; $[\alpha]_D^{20} -32^\circ$ (EtOH); MS (on methyl ester): m/e 364 M^+ ; 121 (100%); dicyclohexylamine salt: m.p. 204°]. This dicarboxylic acid may also be directly isolated from the oleoresin by extraction with a saturated solution of $NaHCO_3$.

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The identification of the methyl esters of the four acids was achieved by direct comparison with authentic samples (TLC, GLC, i.r. and MS).

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MYRISTICACEAE

TRIGLYCERIDES OF THE SEEDS OF *MYRISTICA OFFICINALIS*

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Plant. *Myristica officinalis* Mart.

Source. State of Rio de Janeiro, Brazil.

Uses. As a folk remedy against arthritis.¹

Previous work. None.

Seeds. Extracted with hot EtOH. On cooling, a white precipitate was obtained (13% of dry seed weight), which, after recrystallization from EtOH, showed m.p. 43–5° (uncorrected) and was constituted of only triglycerides² (TLC, light petrol (40–70)–ethyl ether–MeOH–AcOH—90:7:2:0.5). These were saponified with KOH, the fatty acids were methylated (BF₃ in MeOH) and methyl esters sepd by GLC (20% EGS column, 170°) showing the following composition:³ less than 9C: 4.06%; 9:0: 0.30%; 10:0: 0.40%; 12:0: 20.30%; 12:1: traces; 14:0: 66.45%; 14:1: 2.07%; 16:0: 4.27%; 17:0: 1.10%; 18:0: 0.54%; 19:0: 1.60%.

GLC peaks were identified by direct comparison with authentic standards and by carbon number theory.⁴

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