

Composition of the Essential Oil from *Cedrela odorata* L

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Synopsis—The essential oil from *CEDRELA ODORATA* L. was analysed by a combination of various CHROMATOGRAPHIC METHODS, FRACTIONAL DISTILLATION and GLC/MS. EIGHTEEN SUBSTANCES of predominantly SESQUITERPENIC CHARACTER were identified. The presence of another seven substances which were tentatively characterized, was also established.

The essential oil from *Cedrela odorata* has a characteristic agreeable dry-woody powerful odour, and to some extent its odour reminds one for example of the essential oil of cedar-wood or some species of cyperus oils. It is used mainly for the perfuming of soaps, certain sprays, desinfectans etc. Its organoleptic properties and its use are described in greater detail by Arctander (1). It is prepared from the wood of the tree *Cedrela odorata* L. (Meliaceae), often from the waste material left over when this is made into cigar boxes, cabinets, etc. The main production area is Brazil where it grows in the jungles of Paraná, Sta Cantarina and Rio Grande do Sul states. The estimation of annual production in Brazil, which is its most important producer, is between 500 and 700 kg. Smaller amounts are also produced in the Caribbean area and Central America.

Except for the isolation of the sesquiterpenic alcohol cedrelanol (2), identical with the formerly described pilgerol (3) and δ -cadinol (4), no other data are to be found in the literature concerning the chemical composition of this essential oil. For our analysis we made use of an authentic sample of a Brazilian essential oil** which had d_4^{20} 0,9189, n_D^{20} 1,4994 and $[\alpha]_D^{20} - 2,7^\circ$. Since according to preliminary analyses, the oil contains almost exclusively sesquiterpenic hydrocarbons and sesquiterpenic alcohols, we first separated the

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essential oil chromatographically to the groups of compounds mentioned. During this adsorption chromatography we also succeeded in isolating and identifying three crystalline alcohols: cadinenol [(±)-epicubenol] (Fig. 1) (5), juniper camphor (Fig. 2) (6) and amorphan-3-ene-9β-ol (Fig. 3) (7). The last mentioned alcohol is identical with so called cedrelanol (in older literature other names may be found for this alcohol, as for example torreyol, albicaulol, pilgerol, δ-cadinol). The fourth sesquiterpenic alcohol, accompanied during chromatography tenaciously by traces of two additional substances, could not be purified up to the present time; according to PMR data the substance could be T-muurolol (Fig. 4) (8). The essential oil contains about 18% of oxygen containing compounds.

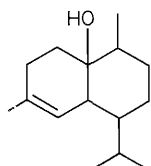


Figure 1

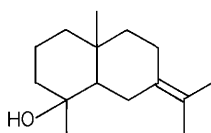


Figure 2

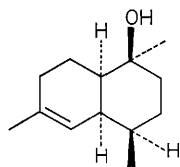


Figure 3

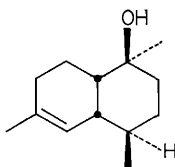


Figure 4

In view of the fact that the obtained mixture of sesquiterpenic hydrocarbons contained according to GLC analysis on a capillary column 24 components, we first carried out its fractional distillation under GLC control. The selected fractions were further separated by column chromatography on silicagel containing silver nitrate, and obtained single fractions were identified by means of GLC/MS and comparison with standard samples. In the first distillation fraction traces of lower hydrocarbons were detected: p-cymene, 2-phenylpentane, 1-methyl-4-(2-butyl)-benzene, unidentified hydrocarbons $C_{12}H_{16}$ and $C_{12}H_{18}$ as well as a methyl ether $C_{11}H_{14}O$. In the lowest boiling fractions already containing sesquiterpenic hydrocarbons α -cubebene and (-)- α -copaene were present. The subsequent fractions contained α -maaliene as the main component. We also identified these substances by IR spectra; α -maaliene was also identified on the basis of the IR spectrum of its saturated skeleton. According to GLC/MS, α -curcumene, β -bisabolene, cuparene, α -muurolene, δ - and γ -cadinene, S-guaiazulene, and most probably also β -cadinene were present in the middle fractions. In the highest boiling fractions we could find α -cedrene, calamenene and α -calacorene. Another ca-

lacorene and the hydrocarbon $C_{15}H_{24}$, probably of the amorphane type, could not be identified, due to the lack of reference substances and published spectra.

The detected substances, representing the main components of the essential oil, probably are not the carriers of the typical odour of this essential oil. In order to identify the odouriferous principle a larger amount of the analysed essential oil or the wood extract would be required.

EXPERIMENTAL

The measurement of the IR spectra was carried out on a Zeiss UR 10 spectrophotometer, PMR spectra were recorded with a Varian-100 apparatus using TMS as internal standard. For analytical GLC a Perkin-Elmer Model F 11 chromatograph, provided with FID, was employed. For GLC/MS a gas chromatograph of the Pye 104 series was used, which was connected with a MS AEI 902 mass spectrometer. For column chromatography silica gel deactivated with 11% of water or impregnated with 12% of silver nitrate was used. For TLC silica gel G (Merck) was used. The mass spectra were compared with the published ones (9) (10) or with the spectra of reference samples.

Chromatography of the essential oil

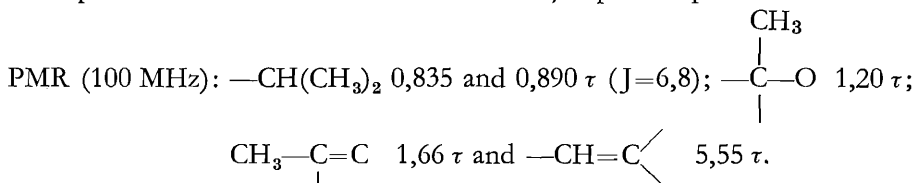
The essential oil from *Cedrela odorata* (83,3 g) was chromatographed on 1500 g of deactivated silica gel. The course of the chromatography is represented in the *Table*.

Table

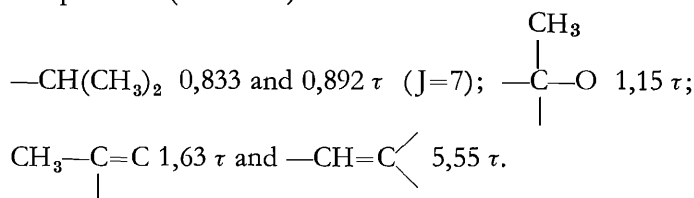
Fraction	Eluent	Weight in g	Main component
1	light petroleum	67,6	
2	light petroleum	0,9	mixture of C_{15} hydrocarbons cadinenol (\pm epi-cubenol)
3		1,0	
4		2,8	
5	light petroleum +8% of ether	3,7	
6		2,1	juniper camphor
7		4,1	amorphan-3-ene-9 β -ol
8		1,1	

Cadinenol (\pm epi-cubenol): crystals of m. p. $75^\circ C$ (light petroleum), $[\alpha]_D^{20}$ $-2,8^\circ$ ($c=0,5$, $CHCl_3$); IR identical with a published spectrum (6), PMR spectrum in agreement with the proposed structure. $C_{15}H_{26}O$: on rechromatography of the fraction 5 (*Table*) on a hundredfold amount of deactivated

silica gel, using 10% of ether in light petroleum for elution, a very viscous liquid was obtained which according to TLC (20% of ether in light petroleum) contained in addition to the main component traces of a product more polar than cadinenol but different from juniper camphor.



T-muurolol (8) PMR spectrum (100 MHz):



Juniper camphor: crystals of m. p. 168,5°C (light petroleum); $[\alpha]_D^{20} \pm 0^\circ$; mol. weight: 222 (MS); IR spectrum identical with the published data (6).

Amorphan-3-ene-9 β -ol: crystals of m. p. 138° (light petroleum); $[\alpha]_D^{20} -112,7^\circ$ (CHCl₃, c=0,16); IR spectrum identical with the published data (6), MS also identical with the published data (9).

Distillation of sesquiterpenic hydrocarbons

The chromatographic fraction 1 (67,6 g) was submitted to fractional distillation at 3 Torr on a glass column containing an organised filling (40 theoretical plates) and using a 1 : 50 reflux ratio. Fractions of 1 ml were collected (total 60 fractions). The distillation course was followed by GLC, using a 50 m capillary column, 0,2 mm i. d., made of stainless steel and coated with Carbowax 20 M; temperature 120°C, nitrogen as carrier gas.

(-)- α -Copaene and α -cubebene: the distillation fraction No 3 (900 mg) was chromatographed on argentised silica gel (50 g) with light petroleum. From the first fractions (-)- α -copaene (IR, MS) was obtained, from subsequent fractions α -cubebene (IR, MS) was isolated.

α -Maaliene: distillation fraction 21—25 was chromatographed on argentised silica gel, analogously to the mixture of α -copaene and α -cubebene. The medium fractions contained pure α -maaliene, IR spectrum identical with the published data (11).

Maaliene: conventional hydrogenation on platinum in acetic acid gave a product which had an IR spectrum identical with the published spectrum (11).

Conditions for GLC/MS measurements

Pye 104: all glass column, length 3 m, 1/4" o. d., Chromosorb G wetted with 5% Apiezon L as stationary phase, temperature 170°C, carrier gas helium.

MS AEI 902: electron energy 70 eV.

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