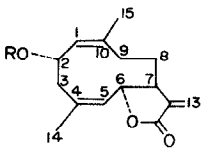
pretierbar, da bedingt durch die Flexibilität des *cis,cis*-Cyclodecadiens ein Gemisch verschiedener Konformationen vorliegt. Jedoch wird auch hier das Spektrum bei erhöhter Temperatur in Deuteriobenzol sehr viel schärfer strukturiert. Durch Entkoppelungsexperimente, auch unter Zusatz von $Eu(fod)_3$, beim Acetat des Naturstoffs läßt sich die Konstitution und Konfiguration klären. Alle Daten sind am besten vereinbar mit dem Vorliegen des Lactons **1**.



1: R=H
2: R=Ac

EXPERIMENTELLES

IR. Beckman IR 9, in CCl_4; ^{1}H-NMR: Varian XL 100, δ-Werte, TMS als innerer Standard; MS: Varian MAT 711 mit Datenverarbeitung 70 eV, Direkteinlaß. 1 kg frisch zerkleinerte oberirdische Pflanzenteile extrahierte man mit E–PE (1:2) und trennte den erhalten Extrakt nach Abtrennen methanolunlöslicher gesättigter Kohlenwasserstoffe zunächst durch Säulenchromatographie (Si gel, Akt. St. II) und weiter durch DC (Si gel, GF 254). Als Laufmittel dienten E–PE-Gemische. Mit PE erhielt man 50 mg α-Farnesen und 50 mg Caryophyllen sowie mit E–PE 1:1 120 mg **1**.

cis,cis-2α-*Hydroxycostunolid* (**1**). Zähes, farbloses Öl, IR: OH 3620; γ-Methylenlacton 1770, 1660 cm^{-1}. 100 mg **1** in 0.5 ml Ac_2O und 0·1 ml absol. Pyridin und 10 mg 4-Pyrrolidinopyridin [2] erwärmte man 30 min auf 60°. Nach Zugabe von Ether wurde neutralgewaschen und der Eindampfrückstand durch DC (E–PE 3:7) gereinigt. Man erhielt 100 mg **2**, farbloses Öl, IR: OAc 1750, 1240; γ-Methylenlacton 1770, 1660 cm^{-1}. MS: M^+ *m/e* 290. 153 (2,5%) (ber. für $C_{17}H_{22}O_4$ 290.152); $-H_2C{=}C{=}O$ 248 (10); –AcOH 230 (74); 230–Me 215 (27); $MeCO^+$ 43 (100).

Table 1. ^{1}H-NMR-Daten für **2** (C_6D_6, TMS als innerer Standard, δ-Werte)

30°	120°		Δ†	*J* (Hz)
1 -H	*d(br)*	4.60	0 13	1.2 ~ 5
2β-H	*ddd*	6.20	0.41	1.15 ~ 1
3α-H	*m*	1 5–2.2	–	2 3α = 10
3β-H	*m*	2.65	0.19	2.3β ~ 3
5 -H	*d(br)*	4.60	0.18	3α,3β ~ 13
6β-H *t(br)* 5.20	*dd*	5.17	0.48	5.6β = 10
7α-H	*ddddd*	2 75	0.37	6β,7α = 9
8,9-H	*m*	1.5–2.2	–	7α,8 ~ 10
13-H *s(br)* 6·40	*dd*	6.35	0.76	7α,8′ = 3
13′-H *s(br)* 5·63	*dd*	5.64	0.38	7α,13 = 3
14-H	*s(br)*	1.32	0.16	7α,13′ = 3
15-H	*d*	1.45	0.09	13.13′ = 1.5
OAc *s* 1·61	*s*	1.69	0.18	

* Alle nicht angegebenen Signale sind sehr breite Multipletts.
† Nach Zusatz von ~0.1 äquivalenten $Eu(fod)_3$.

Neben **1** isoliert man α-Farnesen und Caryophyllen.

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POLYPHENOLS AND TRITERPENOIDS OF *EUGENIA GUSTAVIOIDES* WOOD

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Key Word Index—*Eugenia gustavioides*; Myrtaceae; wood extractives; polyphenols, triterpenoids; ellagic acid; maslinic acid.

Difficulties are encountered in gluing *Eugenia gustavioides* F. M. Bail (grey satinash or watergum) during the manufacture of plywood [1]. This investigation was undertaken to identify the components responsible. Ellagic acid was isolated as the major polyphenol and maslinic acid, two unknown triterpene acids (**1**, **2**) and probably tirucallol (**8**) were also present in MeOH extractives. Ellagic acid was identified by comparison with an authentic sample and maslinic acid by comparison of its physical and spectral data with published data [2,3].

IR, NMR and MS data indicated that the two unknown triterpene acids belong to the olean-12-en-28-oic acid series but have different hydroxyl substitutions in rings A and B [4–6]. TLC, GLC and IR revealed that unknown **1** was very similar to arjunolic acid. Furthermore, the MS data of the monomethyl ester showed the same fragments as those of methyl arjunolate. The most common hydroxy substitution in triols of this series seems to be in the C-2, C-3 and C-23 position but unknown compound **1** was not identical with any known compounds, e.g. arjunolic acid, bayogenin, or the methyl ester with methyl 2α, 3α, 23-trihydroxy olean-12-en-28-oate [7].

The NMR spectrum of unknown **2** showed signals

corresponding to severn *tert.* C-methyl groups. TLC, GLC and IR revealed that unknown 2 is very similar to oleanolic acid and the MS data of the monoacetate showed exactly the same fragments as those of oleanolic acid monoacetate. Furthermore, the NMR spectra showed that one proton of unknown 2 at δ3.44 ppm was shifted to the lower field at δ4.68 ppm (t, J = 8 Hz) after acetylation. However, the compound (mp 247–249°) was not identical with any known 3-monohydroxy compounds, e.g. oleanolic acid (mp 305–310°) or 3-epi-oleanolic acid (mp 298°). A dimorphic form of oleanolic acid was not proved in this case.

The IR spectrum of the third unknown indicated that it is a tetracyclic triterpene and with mp 133–134°; it is probably tirucallol (mp 133–134.5[8]) but its identity could not be confirmed owing to the unavailability of authentic sample.

EXPERIMENTAL

The wood sample was collected near Cairns, Queensland. Ground heartwood (3.5 kg) was extd with MeOH (3 days) and the extract concentrated in vacuum. A crystalline ppt. (32 g) was collected, recrystallized from hot MeOH and identified as ellagic acid by direct comparison with an authentic sample [9]. The ether soluble neutrals (14 g) were obtained from the MeOH filtrate after washing with 5% $NaHCO_3$ and sat. Na_2CO_3 solutions successively. The Et_2O soluble neutrals (3.7 g) were chromatographed on thick TLC (Si gel GF_{254}, 0.75 mm thickness) plates with EtOAc–$CHCl_3$–HCOOH, (2:10.1) to give 5 opaque bands with R_f values of 0.20 (fraction 1), 0.29 (2), 0.38 (3), 0.63 (4) and 0.72 (5). After repeated crystallization, finally, fraction 1 (unknown **1**; 115 mg), 2 (maslinic acid; 82 mg), 4 (unknown **2**; 113 mg) and (probably tirucallol; 20 mg) were obtained.

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STEROLS AND TRITERPENES OF *ILEX AQUIFOLIUM*

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Key Word Index—*Ilex aquifolium*; sterols; triterpenes; 24-ethylcholesterol.

Abstract—Sterols of male and female flowers from *Ilex aquifolium* were found to be mainly 24-ethylcholesterol, with trace amounts of cholesterol, 24-methylcholesterol and 24-ethyl-5,22-cholestadien-3β-ol. Several pentacyclic triterpenes were partially characterized.

INTRODUCTION

The involvement of sterols in the flowering process has been inferred from work by Bonner *et al.* [1] and Biswas *et al.* [2]. To our knowledge no study of the sterols of flowers placing emphasis on sexual differentiation has been recorded. *Ilex aquifolium* (holly) is a dioecious species and we report here on the sterols of flowers and leaves of male (staminate flowers) and female (carpellate flowers) trees of this species.

RESULTS

GLC data on sterol-triterpene fractions from holly harvested from two locations are summarized in Table 1. Identification of sterols was by comparison of GLC and MS data with those from authentic sterols and with literature data [3]. The principal sterol in all cases was 24-ethylcholesterol (80% of all the sterol in all cases examined). This compound is presumed to be sitosterol although no evidence for the stereochemistry at C-24 is presented. With the same reservations, the other sterols were identified as stigmasterol (10%), campesterol (4%) and cholesterol (trace). Only in male flowers could 24-ethylidenecholesterol be detected (by GLC and MS), in all other cases peaks at this point in the chromatograms appeared by MS to be triterpenes of the oleanane type (*m/e* 218 as base peak) [4].

Leaves also presented similar chromatograms from both types of tree but in these cases a considerable amount of triterpene (presumably oleanane skeletons, as all had base peaks in their mass spectra at *m/e* 218) was present overlapping on TLC with the sterol fraction.

DISCUSSION

No consistent differences in sterol-triterpene composition between flowers or leaves from male or female trees could be noted except possibly for the presence of 24-ethylidenecholesterol in the first harvest of male flowers. This could represent newly synthesized sterol not yet fully reduced to sitosterol or else could be associated with anthesis, since compounds with unsaturated side-chains occur frequently in large amounts in pollen [5].