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SHORT COMMUNICATION

TRITERPENOIDS ISOLATED FROM *MACHAERIUM INCORRUPTIBILE*

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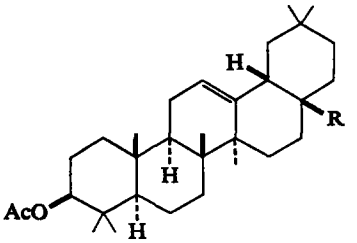
Abstract—A biogenetic oxidative sequence is illustrated by the isolation of four structurally related triterpenoids (I–IV) from *Machaerium incorruptibile*.

IN CONTINUATION of our studies[1–3] of Brazilian members of the *Leguminosae* family, we have examined the sapwood of *Machaerium incorruptibile* Fr. Allem.[4] This tree is one of the Brazilian Jacarandás and it grows in the wet forests of the coastal mountain regions of southern Brazil. Chromatographic examination of the benzene extract of the sapwood yielded four substances that have been identified as β-amyrin acetate (I), erythrodiol 3-acetate (II), *O*-acetyl-oleanolic aldehyde (III), and *O*-acetyl-oleanolic acid (IV).



(I) R = CH_3
(II) R = CH_2OH
(III) R = CHO
(IV) R = CO_2H

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TABLE 1. SIGNIFICANT PEAKS AND SIGNALS IN THE INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE COMPOUNDS (I–IV)

Compound	M.p.	Lit. m.p.	Infrared spectra (KBr disk) ν_{max} cm^{-1}	Assignments of NMR spectra (60 Mc/s in $CDCl_3$)										
								Signals due to tertiary C-methyl groups						
				CH_2–CH=C	AcO–CH–CH_2	CH_2–CH–C	AcO–	Total number	Chemical shifts and relative integrals					Additional signals
β-Amyrin acetate (I)	240–242°	241°	1740 1250 814	4·72 t*	5·45 t $J=7$	Multiplet centred at 7·18	7·97	8	8·72 [2]	8·86 [1]	9·06 [2]	9·13 [2]	9·23 [1]	
Erythrodiol acetate (II)	237–239°	238·5–239°⁶	3600 1730 1270 818	4·85 t*	5·54 t $J=7$	—	8·04	7		8·93 [1]		9·14 [2]	9·23 [4]	AB system (6·48 and 6·87, $J=12$) due to >C·CH_2OH
O-Acetyl-oleanolic aldehyde (III)	225–226°	225–228°	2740 1735 1250 822 broad	4·64 t*	5·49 t $J=7$	Multiplet centred at 7·35	7·97	7		8·86 [1]	9·07 [3]	9·14 [2]	9·27 [1]	Singlet (0·58) due to >C–CHO
O-Acetyl-oleanolic acid (IV)	259–260	264–265°¹⁷	1740 1250 820	4·72 t*	5·50 t $J=7$	Multiplet centred at 7·18	7·97	7		8·87 [1]	9·07 [3]	9·14 [2]	9·25 [1]	Broad band due to –CO_2H not observed

Chemical shifts are given on the τ scale. Coupling constants, J, are in c/s. t = triplet; t* = incompletely resolved triplet.

The identification of these four substances (I–IV) involved initially the examination of their I.R. and NMR spectra. The significant I.R. peaks and NMR signals are summarized in Table 1. These spectra showed some striking correspondences, including the fingerprint region of their I.R. spectra, and this suggested that the four compounds belonged to one structural type. Points of similarity included the presence of (*a*) sharp singlets (τ 7·97–8·04) in the NMR spectra and ester carbonyl absorption (ν_{max} 1740–1730 cm^{-1}) to be associated with one acetoxyl group, (*b*) triplets (τ 5·45–5·54; J=7 c/s) associated with one proton in the grouping AcO—CH—CH_2—, (*c*) one vinyl proton appearing as a broad triplet (τ 4·64–4·85) split by two allylic protons (multiplet $\sim \tau$ 7·2), and (*d*) seven tertiary methyl groups. This immediately suggested that the four substances were possibly pentacyclic triterpenoids of the β-amyrin type in which the acetoxyl group was placed in the 3-position.

Differences between the I.R. and NMR spectra of the four compounds were interpreted as follows. Compound (I) showed one tertiary methyl group in addition to the seven shown by the other three substances, and it was identified as β-amyrin acetate (I). Compound (II) showed a sharp hydroxyl band (ν_{max} 3600 cm^{-1}) in its I.R. spectrum and an AB system (τ 6·48 and 6·87; J=12 c/s) to be associated with a —CH_2OH group bonded to an asymmetric tertiary carbon atom.[5] The identification of this substance as erythrodiol 3-acetate (II) was confirmed by its acetylation to give erythrodiol diacetate.[6] Compound (III) was identified as *O*-acetyl-oleanolic aldehyde which we had previously isolated from *Machaerium scleroxylon*,[2] and compound (IV) as *O*-acetyl-oleanolic acid.

Djerassi[7] has already commented on the occurrence of β-amyrin, erythrodiol, oleanolic aldehyde,[8] and oleanolic acid in different plants belonging to the Cactaceae. Although these substances were isolated from different plants, it was nevertheless reasonable to assume[7] that the biogenetic relation between these triterpenoids involved the same type of oxidative sequence (R—CH_3 → R—CH_2OH → R—CHO → R—CO_2H) as proposed by Bloch[9] to be involved in the mammalian transformation of lanosterol to cholesterol. There is now good evidence[10] that the biosynthetic transformations of triterpenoids follow similar courses in plants and in animals, and this receives good support from the recent isolation from plants of various partially methylated steroids including macdougallin,[11] cycloeucalenol,[12] cyclobuxine,[13] and lophenol.[14]

Thus the isolation of compounds (I, II, III, and IV) from a single plant source belonging to the Leguminosae may be regarded as illustrating an acceptable biosynthetic sequence in plants. The Leguminosae is usually characterized by the presence of isoflavonoids,[15]

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rotenoids,[16] and neoflavanoids[1–3] as natural products, so it may be noted that *O*-acetyl-oleanolic acid (IV) has also been isolated[17] from *Pterocarpus angolensis* (*Leguminosae*). So far as we are aware, erythrodiol 3-acetate (II) has not been recognized previously as a natural product.

EXPERIMENTAL

Extraction of Machaerium incorruptibile *Sapwood*

Isolation of β-amyrin acetate (I), *erythrodiol 3-acetate* (II), O-*acetyl-oleanolic aldehyde* (III), *and* O-*acetyl-oleanolic acid* (IV). The ground, dried sapwood (1500 g) was continuously extracted with benzene for 40 hr. Removal of the benzene under diminished pressure gave a residue (28 g) which was dissolved in benzene (150 ml) and chromatographed on silica gel (600 g). Successive elution with benzene, benzene–chloroform mixtures, and then chloroform, and examination of the eluates by thin-layer chromatography gave four main fractions which were purified further by a combination of fractional crystallization and chromatography. This eventually yielded β-amyrin acetate (I) (440 mg) as colourless needles, m.p. 240–242°, $[\alpha]_D = +79°$ (*c*, 4·0; $CHCl_3$) from light petroleum (b.p. 60–80°; erythrodiol 3-acetate (II) (82 mg) as colourless needles, 237–239°, $[\alpha]_D = +71°$ (*c*, 4·4; $CHCl_3$), from chloroform–methanol; *O*-acetyl-oleanolic aldehyde (III) (690 mg) as colourless needles, m.p. 225–226°, $[\alpha]_D = +57°$ (*c*, 6·6 $CHCl_3$) from methanol and *O*-acetyl-oleanolic acid (IV) (43 mg) as colourless needles, m.p. 259–260°, $[\alpha]_D = +74°$ (*c*, 4·0; $CHCl_3$) from methanol.

The identity of β-amyrin acetate (I), *O*-acetyl-oleanolic aldehyde (III), and *O*-acetyl-oleanolic acid (IV) were confirmed by comparison with authentic samples. Erythrodiol 3-acetate (II) was characterized by acetylation with acetic anhydride–pyridine at room temperature yielding erythrodiol diacetate, m.p. 186° (lit.[6] m.p. 186°), identical with an authentic specimen.

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