labelled ethanol, whereas ^{1}H-NMR studies[7,8] on the camphanoyl derivatives confirmed the *pro-R* absolute configuration of the exchanged hydrogen atom.

The above results opened the way to synthetise the required (**1***R*) [1-^{3}H, ^{2}H$_1$] 3-phenylpropanol, using sodium borotritiide as primary ^{3}H source. Thus, incubation of (**1***S*) [1-^{2}H$_1$] 3-phenylpropanol (4, $H_S = {}^2H$), 99% d_1, 10 mmoles, with (**1***RS*) [1-^{3}H] ethanol, 1 mmole, about 100 mCi, obtained upon NaB^{3}H$_4$ reduction of acetaldehyde, gave (**1***R*) [1-^{3}H, ^{2}H$_1$] 3-phenylpropanol (4, $H_R = {}^3H$, $H_S = {}^2H$), 4.5 mCi/mmole, 99 d_1, in nearly quantitative chemical and overall acceptable radiochemical yields. Conversion to (**4***R*) [4-^{3}H, ^{2}H$_1$] D,L-homoserine and to the (**4***S*)-isomer was carried on as reported[5] and proceeded without tritium loss.

Repetition of this type of experiments, using [1-^{2}H$_2$] 2-phenylethanol or unlabelled **3** and [1-^{2}H$_2$] ethanol, indicated a negligeable isotopic exchange, thus suggesting that at present the labelling procedure reported is unsuitable for the synthesis of ^{3}H, ^{2}H-asymmetrically labelled serine if a high ^{3}H-specific activity is required. However, since (**1***S*) [1-^{2}H$_1$] 2-phenylethanol (3, $H_S = {}^2H$) is obtained in growing cultures of *Willia anomala* Hansen from [1-^{2}H$_2$] 2-phenyl ethylamine through a process which we now know from experiments with asymmetrically labelled amine to involve removal of the *pro-R* hydrogen atom from the position α to the nitrogen atom, followed by reduction of the intermediate phenylacetaldehyde, experiments designed to introduce tritium in the C_6–C_2 alcohol in the reduction step are in progress.

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A p-menthane derivative isolated from culture filtrates of *Fusicoccum amygdali*, Del.

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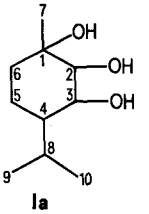
Summary. From culture filtrates of *Fusicoccum amygdali*, Del., a new compound, whose structure corresponds to 1,2,3-trihydroxy-p-menthane, has been isolated. Its discovery is of some interest since, to our knowledge, it is the first time that a monoterpenoid is isolated from a microorganism.

Submerged cultures of *Fusicoccum amygdali*, Del. have been known to produce fusicoccin[3], a highly phytotoxic diterpene glucoside, along with a number of closely related co-metabolites[4–11], each with a characteristic diterpene aglycone. An extremely careful separation of the components of culture filtrates allowed us to isolate an entirely different, novel compound possessing the para-menthane skeleton. Spectroscopic and chemical evidence reported below showed it to be of structure **I**. To our knowledge, this is the 1st case that a monoterpenoid had been isolated from cultures of a microorganism. Further studies, however, are required to ascertain whether or not **I** represents a true metabolite of *Fusicoccum amygdali*, Del.



Ia

Compound **I** was obtained in low (0.5%) yields by extensive and repeated chromatographic fractionation of the residue left in ethyl acetate after crystallization of the major metabolite. Several crystallizations from benzene of the newly isolated product gave white prisms m.p. 86–87 °C. Its molecular formula $C_{10}H_{20}O_3$ resulted from elemental analysis. The IR-spectrum (CCl_4) showed sharp bands at 3625 and 3575 cm^{-1} indicating the presence of at least 2 alcoholic functions. The ^{1}H-NMR-spectrum (in a 3:1 mixture of $CDCl_3$ and DMSO-d_6, at 100 MHz) revealed the presence of 2 secondary and 1 tertiary hydroxyl groups. It also showed that the molecule has 1 secondary isopropyl and 1 tertiary methyl group and, furthermore, has a fully saturated hydrocarbon backbone.

The above findings may readily be accomodated in the monoterpenoid structure **Ia** with the following assigned ^{1}H-NMR-parameters: $\delta_{CDCl_3 + DMSO} = 0.98$ (6H, d, 6.7 Hz 9 $-CH_3$, 10 $-CH_3$); 1.32 (3H, s, 7 $-CH_3$); 1.66 (1H, m, C_8-H); 3.13 (1H, d, 4 Hz, exchangeable, C_3 –OH); 3.33 (1H, s, exchangeable, C_1 –OH); 3.45 (1H, dd, 3 Hz, 4.8 Hz, C_2 –H); 3.79 (1H, d, 3 Hz, exchangeable, C_2OH); 4.03 (1H, ddd, 2 Hz, 4 Hz, 4.8 Hz, C_3 –H) ppm. The stereochemistry of the molecule was derived on the basis of the following arguments.

The magnitude of the vicinal coupling constant J_{34} (2 Hz) suggests that the substituents at C_3 and C_4 are cis oriented. In fact, assuming that conformational free energies of substituents in **Ia** are nearly additive (2.15, 1.7 and 0.7 kcal·mole^{-1} for iPr, CH_3 and OH groups, respectively[12]), trans diaxial arrangement of C_3 and C_4 substituents must be greatly destabilized, whereas their diequatorial orientation is expected to result in a much higher value of J_{34} (approx. 8–10). Among the possible 2 cis conformers, the 1 with axial iPr and equatorial C_3 –OH would again give rise to a greater J_{34} (approximately 5 Hz) and, also the

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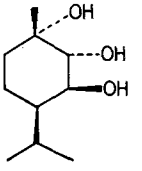
corresponding conformational state most probably would have a low population. Hence, in the favored cis arrangement, the iPr group is equatorial and the C_3 –OH axial. The relative orientation of C_3 –OH and C_2 –OH groups follows from the observed value of J_{23}. Vicinal diols are known to exhibit 5.6 and 2.3 Hz 3-bond ^{1}H-^{1}H couplings for rela-



I

tive orientations of the OH groups that correspond, respectively, to the trans diaxal and cis arrangement in a non-distorted cyclohexane skeleton[13]. The measured value of 4.8 Hz therefore suggests that both C_3 –OH and C_2 –OH are axial. Further corroboration to this conclusion was provided by the magnitude of the 2 J_{HCOH} couplings (3 and 4 Hz, respectively, for C_2 –H and C_3 –H). These couplings are known to depend on the preferred rotational orientation of the OH group which, in turn, reflects its steric interactions with neighbouring groups[14]. In vicinally di- and tri-substituted 6-membered ring systems equatorial hydroxyl groups usually exhibit a higher (6–7 Hz) J_{HCOH} couplings, whereas axially oriented OH groups systematically show lower values (3–4 Hz)[15].

^{1}H-NMR furnished no direct information regarding the orientation of the substituents at C_1, although the linewidth of the 7–CH_3 protons (1.6 Hz) suggested the occurrence of a 4-bond W-coupling with one of the C_6 methylene protons, typical of axially oriented methyl groups[16].

The stereochemistry at C_1 was conclusively demonstrated by converting the new product into its acetonide and subsequent acetylation of the latter. ^{1}H-NMR showed the acylable OH to be at C_3, i.e. the acetonide formation occurred with the participation of C_1 –OH and C_2 –OH. Since the stereochemistry of this reaction requires that the 2 alcoholic functions be cis one to another, in the preferred conformation the OH group at C_1 must be equatorial and the C_1-methyl axial.

The stereochemistry of the molecule is displayed by **I**. Synthesis of the racemic menthane triols is in progress and will be reported in a separate publication.

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A new furanoid fatty acid from the soft corals *Sarcophyton glaucum* and *gemmatum*

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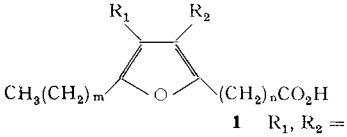
Summary. The isolation and spectral data of a new furanoid fatty acid obtained from 2 *Sarcophyton* soft-corals is reported.

Most recently, the isolation from fish lipids of a whole series of furane containing long-chain fatty acids, of the general structure **1**, have been reported[1].



1 $R_1, R_2 = H, CH_3$ m = 2–5 n = 7–12
1a $R_1, R_2 = CH_3$ m = 4 n = 2
(Me-ester)

We wish to represent here the isolation for the 1st time of a new member of this series **1a** ($R_1 = R_2 = CH_3$, m = 4, and n = 2, as the Me-ester in about 0.04% dry weight) from a different marine organism namely, from a soft coral. Compound **1a** could be revealed in the petrol-ether fraction of 2 species of *Sarcophyton*, *S. glaucum* and *S. gemmatum*, while in *S. decaryi* and 2 other *Sarcophyton* sp. it was absent. Compound **1a** has been assigned the methyl 3,4-dimethyl-5-n-pentylfurylpropionate structure on the basis of the following evidence. IR(CCl_4): 1740, 1598w, 1365, 1220, 1168, 1122, 1035, 990, 710 cm^{-1}.UV (MeOH): λ_{max} 225 nm(ε 7,400), positive Ehrlich test for furane rings. NMR ($CDCl_3$, 270 MHz); δ 3,66s(OCH_3), 2.84t (J = 7.6 Hz, 2H)[2], 2.58t (J = 7.6 Hz, 2H)[2], 2.47t(J = 7.6, 2H), 184s(3H), 1.82s(3H), 1.21–1.31m(4H) and 0.88t(J = 7.0 Hz, terminal methyl). ^{13}C-NMR ($CDCl_3$, 22.63 MHz): 173,4s (CO_2Me), 149.2s, 145.9s, 115.5s and 114.7s (the 4 furane ring carbon atoms)[3], 51.5q (OMe), 33.1t, 31.5t 28.4t, 26.1t, 22.5t, 21.8t, 14.0q (the terminal n-pentyl-Me) and 8.3q (the 2 vinylic Me groups). MS: m/e 252.1694 ($C_{15}H_{24}O_3$, M^+, 40%), 195.0993 ($C_{11}H_{15}O_3$, $[M\text{-}C_4H_9]^+$, 100%), 179.1426 ($C_{12}H_{19}O$, $[M\text{-}CH_2CO_2Me]$, 88%) and 135.0797 ($C_9H_{11}O$, 95%). The above data are in good agreement with the suggested substituted furane system[4]; however, the substitution sequence, suggested mainly according to the ^{1}H-NMR[5] and a speculative biosynthesis, demanded further evidence. Warming up of a solution of **1a** with maleic anhydride in benzene for 12 h gave the expected 1:1 adduct. The 2 methyl groups signals observed in the ^{1}H-NMR spectrum (δ 1.67s and 1.68s) established unequivocally the 3,4-position of the Me-groups in **1a**. The isolation of compound **1a** from a soft coral is interesting from the biosynthetic point of view. The suggested 1,4-oxidation of fatty acids, followed by methylation and consequence cyclization to a furane ring, does not seem to be unique for fish and may be a more general transformation which has to be further investigated.

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