Tetrahedron Letters No. 16, pp 1407 - 1410, 1977. Pergamon Press. Printed in Great Britain.

SACCULATAL AND ISOSACCULATAL, TWO NEW EXCEPTIONAL DITERPENEDIALS FROM THE LIVERWORT, *Trichocoleopsis sacculata*

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(Received in UK 1 March 1977; accepted for publication 7 March 1977)

Abstract:

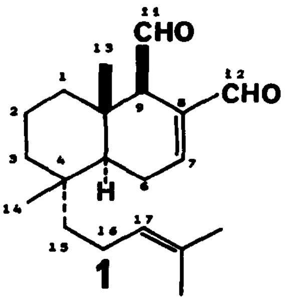
The stereostructures of the two new exceptional diterpene dialdehydes from the liverwort, *Trichocoleopsis sacculata*: sacculatal (1), responsible for the characteristic pungent taste, and isosacculatal (2) have been determined by the spectral evidence and by comparison with polygodial (3), isopolygodial (4), and drimanediol (6) of known relative configurations.

The liverworts, *Porella vernicosa* complex, display skin irritant properties and a particularly intense pungent taste. Recently, we have described that the pungency of *Porella* is due to the sesquiterpene-dial 3[1]. Characteristic pungent substances were also obtained from another liverwort, *Trichocoleopsis sacculata*. We now wish to report the structures of the two novel diterpene-dialdehydes, sacculatal (1) and isosacculatal (2), the former of which is responsible for the pungency of this plant.

Column and preparative thin layer chromatographies on silica gel of the combined ether extracts of the air-dried material (40.6 g) resulted in the isolation of the dialdehydes 1 (0.62 % dry weight of liverwort), mp 65-66°C, $(\alpha)_D$ -31.4° (c, 3.5), and 2 (0.12 %), liquid, $(\alpha)_D$ -145° (c, 1.4), together with the known sesquiterpenes, pinguisone[2] and deoxopinguisone[3].

Sacculatal 1. $C_{20}H_{30}O_2$: High resolution mass spectrometry and microanalysis. The UV (λ_{max}^{EtOH} 231 nm, ε, 11256) and IR bands (2710, 1715, 1670, 1640 and 820 cm^{-1}) and the signals in the NMR spectrum at δ 9.42 (s, 1H), 9.50 (d, J=4 Hz, 1H) and 7.08 ppm (m, 1H) suggested the presence of a disubstituted α,β-unsaturated aldehyde and a simple aldehyde. The arrangement of two aldehyde groups as shown in 1 was supported by the spin decoupling experiments : irradiation at the center of the olefinic multiplet at 7.08 ppm caused the complex signal at 2.35 ppm to collapse to a sharp multiplet and simplified the broad multiplet at 2.78 ppm ; in the reverse irradiation at 2.35 ppm, the signal at 2.98 ppm collapsed to a singlet broadened by long range coupling. Irradiation at the center of the aldehyde doublet at 9.50 ppm collapsed the broad singlet at 2.78 ppm to a broad quartet ; the reverse experiment transformed the aldehyde doublet into a sharp singlet. The NMR spectrum of 1 also showed the presence of the two tertiary methyl (0.95 and 0.96 ppm) and the dimethylallyl groups (1.57 and 1.65 ppm, each broad singlet, 5.02 ppm, m, 1H). The assignment of the latter group was confirmed by double resonance experiments. Further proof of the location of the two aldehyde groups is described below. Sacculatal gave a bis-2,4-dinitrophenylhydrazone (mp 187-188°C ; λ_{max}^{EtOH} 358 nm, ε 38123)[4]. Treatment of 1 with dilute alkali formed an α,β-unsaturated γ-lactone (1760 cm^{-1} ; 3.90 and 4.34 ppm, each triplet, J=9 Hz, 2H, 6.84 ppm, quartet, J=8 Hz, 1H) indicating a 1,4-dialdehyde undergoing an internal crossed Cannizaro reaction[4]. Reduction of 1 with lithium aluminium hydride afforded the corresponding diol 5 (mp 91-92°C ; $(\alpha)_D$ = 15° (c, 0.75) ; 3300, 1035 and 990 cm^{-1}) ; its infrared spectrum was very similar to that of drimane-diol 6. The above results, coupled with the molecular formula, showed 1 to be a bicyclic diterpene.

The extremely similar UV, IR, and NMR spectra (except for the presence of a dimethylallyl group and the absence of a tertiary methyl group) suggest that sacculatal possesses the same drimane type skeleton as polygodial 3, one dimethylallyl group being attached to one quaternary methyl group of 3. Polygodial (3) and drimane diol (6) showed well separated bands at 1390 and 1368 cm^{-1}, and 1390 and 1370 cm^{-1} in IR spectra, respectively, characteristic of the gem-dimethyl groups, while sacculatal showed a simple absorption band at 1380 cm^{-1}, indicating the addition of a dimethylallyl group at one of gem-dimethyl groups. The mass spectrum of sacculatal is in good agreement with the proposed structure and the cracking pattern was fully comparable to that of 3[4]. Full support for structure 1, including the absolute stereochemistry, was confirmed by comparison of the europium shifted NMR spectra[5] between 5 and 6. With increasing concentrations of the shift reagent, the C-10 methyl group of 5 showed the largest down-field shift and the movement was almost the same as for the C-10 methyl group of diol 6. The C-14 quaternary methyl group was shifted moderately and its movement was almost identical to that of the C-14 methyl group (axial) of 6. These results coupled with the simple absorption band at 1380 cm^{-1} indicated that a dimethylallyl group was attached to the C-14 equatorial methyl group. All these data, together with biogenetic considerations, show that the new diterpene aldehyde is most favourably represented by formula 1.



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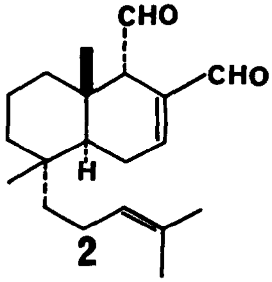

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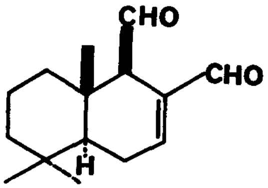

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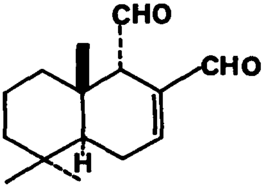

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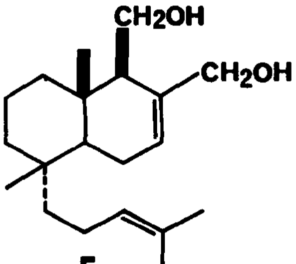

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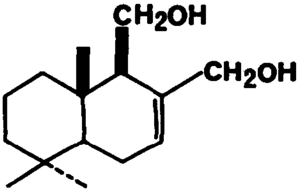

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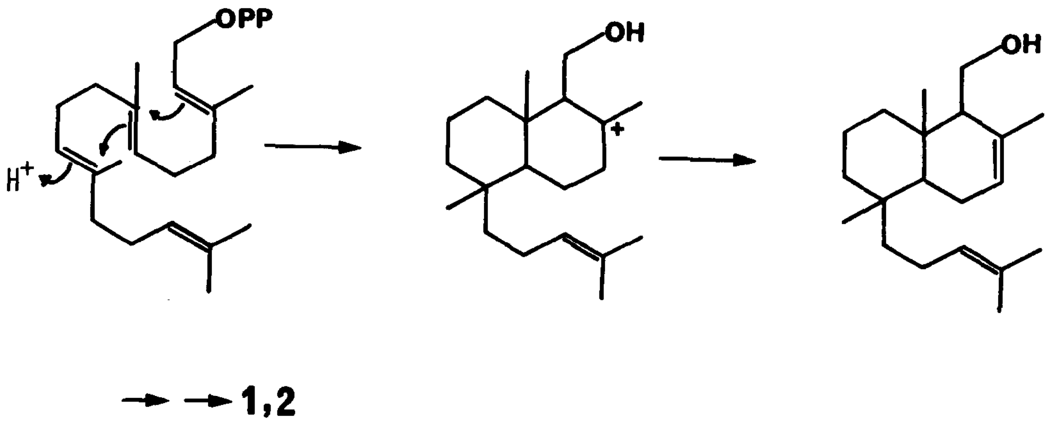
Isosacculatal (2). The physical properties of the less polar diterpene dialdehyde are listed below. $C_{20}H_{30}O_2$ (M^+ 302) ; λ^{EtOH}_{max} 228 nm (ε, 7861), IR 2710, 1720 and 1680 cm^{-1} (α,β-unsaturated aldehyde and simple aldehyde), 1650 and 840 cm^{-1} (trisubstituted double bond) ; 0.93 (s, 3H), 0.98 (s, 3H), 1.59 and 1.67 (bs, each 3H, allylic methyls), 1.77 (m, H-16), 2.2-2.3 (complex m, H-5), 2.4-2.6 (complex m, 2H, H-6), 3.22 (bs, H-8), 5.02 (bt, H-17), 7.04 (q, J=5 Hz, H-7), 9.38 (s, 1H) and 9.83 ppm (d, J=2.5 Hz, 1H). The UV, IR, NMR and mass spectra are quite similar to those of sacculatal (1). This suggests that the compound 2 may be a stereoisomer of 1. The NMR signals[6] of the simple aldehyde group and one proton on carbon bearing aldehyde group are located down-field to those of sacculatal. This indicated that compound 2 was the C-9 epimer of 1 and that the simple aldehyde group was oriented axially,as in isopolygodial (4). The correctness of this conclusion was also confirmed by the direct transformation of 1 to 2. Treatment of 1 with concentrated sulfuric acid gave a non-pungent component, the spectra data of which were completely identical to those of isosacculatal (2).

The sacculatals (1 and 2) are interesting from a biogenetic viewpoint. The ring system is known in drimane-type sesquiterpenes and an isoprene unit has been added. Diterpenes, in general, are formed from geranylgeranyl pyrophosphate. Sacculatals could be derived from such precursor by a cyclization analogous of that of farnesyl pyrophosphate in drimane-type sesquiterpenes (Scheme 1). Pachydictyol[7] and related compounds[8] are also exceptional diterpenes, and a similar biogenetic hypothesis has been proposed for them[7].



SCHEME 1

Some minor related diterpene dialdehydes possessing a hydroxyl group have been isolated and are now currently investigated.

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