

ENT-KAURENE DITERPENOIDS
FROM THE LIVERWORT *Jungermannia sphaerocarpa* HOOK*

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From the liverwort *Jungermannia sphaerocarpa* HOOK the diterpenoids *ent*-11 α -hydroxykauren-15 α -yl acetate (*I*), *ent*-11 α -hydroxykauren-15-one (*II*) and *ent*-kaurene-11 α ,15 α -diol (*III*) were isolated. Their structure was confirmed by X-ray analysis.

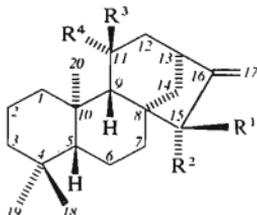
In one of the preceding papers¹ we described the isolation of three diterpenoids from the liverwort *Jungermannia sphaerocarpa* HOOK: hydroxy acetate *I*, hydroxy ketone *II* and diol *III*. The purpose of this communication is to prove the structure of these three substances for which we have demonstrated by chemical correlation that they are compounds with identical skeleton and the same positions of substituents.

Hydrolysis of monoacetate *I* gave a diol, identical according to ¹H-NMR, MS and IR spectra with native diol *III*. Oxidation of keto alcohol *II* and diol *III* with chromium trioxide in pyridine afforded the same diketone *IV*. From the related liverwort *Solenostoma triste* [NEES] K. MÜLL [syn. *J. tristis* NEES] (ref.²) Connolly and Thornton³ have isolated four diterpenoids. The physico-chemical data of our compounds *I*, *II* and *III* agreed with those of three corresponding components from the liverwort *S. triste*. From the comparison of the authentic sample of *ent*-kaurene-11 α ,15 α -diol with our diol *III* it followed that they are identical. The identity was confirmed on the basis of physico-chemical data also in the case of keto alcohol *II* and hydroxy acetate *I*. In extracts from the liverwort *J. sphaerocarpa* the presence of the fourth substance, i.e. (16*R*)-*ent*-11 α -hydroxykauran-15-one (*V*) isolated by Connolly and Thornton³ could not be demonstrated.

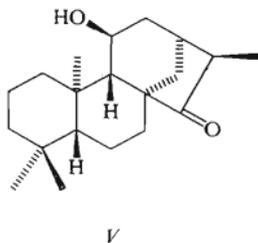
During the hydrogenation of diol *III* on palladium catalyst a rearrangement takes place which is similar to that of garryfoline to cuauchichicine, occurring in the presence of HCl (ref.³). In contrast to this, under the conditions of the classical garryfoline-cuauchichicine rearrangement^{4,5} our diol afforded ether *VI* which is also formed during the measurement of the ¹H-NMR spectrum of diol *III* in CDCl₃ which was not

* Part CCXLV in the series On Terpenes; Part CCXLIV: Parfuem. Kosmet., in press.

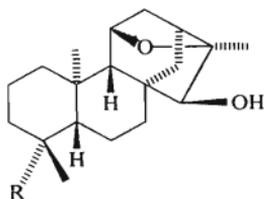
perfectly purified from hydrogen chloride. The fact that native *ent*-11 α -hydroxykauren-15 α -yl acetate *I* cannot be hydrogenated in CH₃COOH also speaks for the structure of ether *VI*. Herz⁷ also mentions the formation of derivative *VII*, similar to our ether *VI*. His case, as well as ours thus represents an exception from the garrifoline-cuauchichicine rearrangement.



- I*; R¹ = OCOCH₃, R² = R⁴ = H, R³ = OH
II; R¹ - R² = O, R³ = OH, R⁴ = H
III; R¹ = R³ = OH, R² = R⁴ = H
IV; R¹ - R² = R³ - R⁴ = O



V



VI; R = CH₃
VII; R = COOH

A final confirmation of structure *III*, proposed by Connolly and Thornton³ for the diol, was made possible by X-ray analysis⁸ of the diol from *J. sphaerocarpa*. Hence, the three diterpenes from *J. sphaerocarpa* are *ent*-11 α -hydroxykauren-15 α -yl acetate (*I*), *ent*-11 α -hydroxykauren-15-one (*II*), and *ent*-kauren-11 α ,15 α -diol (*III*).

The repeated occurrence of diterpenoids with *ent*-kauren skeleton^{3,6} in the liverworts of the order *Jungermanniales* is thus remarkable as a possible chemical character and it will be useful to study its significance.

EXPERIMENTAL

The melting points were measured on a heated microscope stage (Kofler block) and they are not corrected. The IR spectra were measured in CHCl₃ on a Zeiss UR 10 spectrophotometer, the UV spectra were taken on an Optica Milano CF4 apparatus. The CD spectra were measured on a Roussel-Jouan, Model CD 185 Dichrograph in methanol. The mass spectra were taken on

an AEI MS 902 spectrophotometer and the $^1\text{H-NMR}$ spectra in deuteriochloroform were recorded with a Varian HA-100 instrument using tetramethylsilane as internal standard. Silica gel for column chromatography was prepared according to Pitra and Štěrba⁹ and was deactivated with 10% of water. Neutral alumina (Laborchemie Apolda, GDR) was used in the Brockmann¹⁰ activity V. For the isolation and characterization of the isolated diterpenoids see ref.¹.

Diol III. A suspension of LiAlH_4 (109.95 mg) in ether (15 ml) was added dropwise into a solution of the hydroxyacetate (53.46 mg) in 15 ml of ether and the mixture was processed to afford 45 mg of a substance which was identical with the native diol *III* as shown by m.p., IR, MS and $^1\text{H-NMR}$ data.

Diketone IV from diol III. Chromium trioxide (204.9 mg) in pyridine (2.1 ml) was added to a solution of diol *III* (216.2 mg) in pyridine (2.2 ml), the mixture was stirred at room temperature for 72 h, and processed to afford 180.65 mg of a mixture of *III* and *IV* (as shown by TLC), which was chromatographed on a column of silica gel (18.5 g). Elution with benzene gave 121.05 mg of diketone *IV*, m.p. 159–160°C. IR spectra: conjugated 5-membered ketone lacking H in the position α to the carbonyl (1723 cm^{-1}), 6-membered ketone (1698 cm^{-1}), $\text{C}=\text{C}$ (1643 cm^{-1}). UV spectrum, λ_{max} (ethanol): 228 nm ($\log \epsilon 4.08$), plateau 305–320 nm ($\log \epsilon 2.09$). CD spectrum: $\Delta\epsilon_{357} - 0.62$, $\Delta\epsilon_{343} + 2.37$, $\Delta\epsilon_{260} + 0.06$, $\Delta\epsilon_{234} + 5.77$, $\Delta\epsilon_{218} 0$. MS: M^+ 300, $\text{C}_{20}\text{H}_{28}\text{O}_2$; m/e 137, $\text{C}_{10}\text{H}_{17}$. $^1\text{H-NMR}$: 0.82 s, 0.89 s, 1.09 s, each 3 H, $3 \times \text{CH}_3-\text{C}-$; 2.57 t, $J \sim 2.6$, 1 H; 3.23 mt, 1 H, allylic to exomethylene (double resonance); 5.37 bs, 1 H and 5.99 bs, 1 H, exomethylene protons.

Diketone IV from hydroxy ketone II. Chromium trioxide (6.3 mg) in pyridine (0.2 ml) was added dropwise to a solution of *II* (15.46 mg) in pyridine (0.3 ml), the mixture was kept at room temperature for 37 h, and processed to afford 14.12 mg of a mixture of *II* and *IV* (as shown by TLC) which was chromatographed on a silica gel column (1.5 g). Elution with benzene gave 10.05 mg of pure diketone *IV*, identical with the specimen obtained above (m.p., mixed m.p., IR, $^1\text{H-NMR}$ and MS).

Rearrangement of diol III in acid medium. Diol *III* (10.5 mg) in methanol (2.1 ml) and ether (1.05 ml) was treated at 0°C for 3.5 h with concentrated hydrochloric acid (0.42 ml). After evaporation of the solvents and crystallization from ethyl acetate 9.9 mg of ether *VI* were isolated, m.p. 84–85°C. IR spectrum: OH (3540 cm^{-1}), the carbonyl frequency was not visible in the spectrum. MS: M^+ 304 – $\text{C}_{20}\text{H}_{32}\text{O}_2$. $^1\text{H-NMR}$ spectrum: 0.845 s, 0.87 s, 1.1 s, 1.31 s, each 3 H, $4 \times \text{CH}_3-\text{C}-$; 2.88 s, 1 H, C-15 H; 4.29 mt, 1 H, C-11 H; 2.44 bs, 1 H, exchangeable OH. $^1\text{H-NMR}$ (CDCl_3 and trichloroacetylisocyanate): 4.36 C-11 H; 4.45 C-15 H.

The plant material was collected in September 1971, in Rudolfovo, Jizera Mountains, Czechoslovakia, and it was identified by Dr J. Váňa, Botany Department, Faculty of Science, Charles University, Prague, where herbarium samples are also deposited. We thank Prof. J. D. Connolly, Department of Chemistry, University of Glasgow for sending a sample of ent-kaurene-11 α ,15 α -diol. X-ray analysis was carried out by the courtesy of Dr M. Przybylska and Dr F. R. Ahmed, National Research Council, Ottawa, Canada. The $^1\text{H-NMR}$ spectra were measured and interpreted by Dr P. Sedmera, the infrared, ultraviolet and CD spectra were measured by Mr P. Formánek and interpreted by Dr S. Vašíčková. Technical assistance was provided by Miss K. Verešová. We thank all those mentioned.

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