binationen und unter Erhöhung der Dosis auf 50 mg/kp werden im Blut kurzzeitig Wirkstoffkonzentrationen von etwa 1 mg/l erreicht (s. Abb. 1). Auch bei der Pour-on-Applikation von Fenthion und Bayer 9017 am Schaf wurden bereits ähnliche ausgeprägte Abhängigkeiten der percutanen Resorption vom Lösungsmittel beobachtet⁶.

Wie aus Abb. 1 weiterhin beim Vergleich der Ergebnisse für Rind und Schaf hervorgeht, wird Dimethoat beim Schaf schwieriger resorbiert als beim Rind im Vergleich zum Trichlorphon.

Nach intramuskulärer Injektion von 50 mg/kp Dimethoat am Schaf konnten wir im Blut Wirkstoffkonzentrationen von 3–4 mg/l bis zu 8 h p. i. nachweisen; auch daran erkennt man die erschwerte percutane Resorption am Schaf.

Versuche zur Beeinflussung der percutanen Resorption beim Schaf durch Zusatz von Tensiden zur Lösung der Insektizide erbrachten zunächst keine eindeutigen Ergebnisse; in den meisten Fällen konnte keine ausgeprägte Tensidwirkung festgestellt werden. Bei einer speziellen Gruppe von Tensiden zeigte sich jedoch ein interessanter Effekt; bereits in geringen Konzentrationen wird durch diese Substanzen die percutane Resorption von Dimethoat und Trichlorphon am Schaf nahezu vollständig unterdrückt¹³ (die maximalen Wirkstoffkonzentrationen im Blut liegen < 0,1 mg/l). Damit könnten bei minimalen Rückstandsmengen im Körper Wirkstoffzubereitungen zur Ektoparasitenbekämpfung eingesetzt werden, die in der Zukunft im Hinblick auf die ständig geringer festgelegten Toleranzwerte für Insektizidrückstände von Bedeutung sein dürften.

¹³ W. DEDEK u. H. SCHWARZ, DWP 71013 vom 4. 11. 1968.

Absolute Configuration of Carboxyacetylquercinic Acid, Chemical Correlation of Carboxyacetylquercinic Acid with Lanosterol

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We have examined the triterpenoids of *Trametes dickinsii* Berk (Japanese name *Hoorokutake*) (Polyporaceae) and have isolated carboxyacetylquercinic acid and its methyl ester, along with polyporenic acid C and dehydrotumulolic acid of known structures and a new triterpenoid glucoside¹.

ADAM et al.² first isolated carboxyacetylquercinic acid from *Daedalea quercina*. By considering the NMR and mass spectra and on the basis of a few reactions together with a consideration of the known structures

of the coexisting congeners, they assumed this acid to have the structure **1 c**, which still lacks in confirmative chemical evidences.

This paper deals with the chemical correlation of that acid with lanosterol and the establishment of its stereochemistry. The acidic fraction of the MeOH extract of the fungus was subjected to silicagel column chromatography to afford carboxyacetylquercinic acid **1 a**** ($C_{34}H_{53}O_7$, mp 221–224°, $[\alpha]_D + 8.8^\circ$) and carbomethoxyacetylquercinic acid **1 b** ($C_{33}H_{54}O_7$, mp 165.5–167°, $[\alpha]_D + 0.7^\circ$).

1 a was methylated to **1 c**, whose NMR spectrum² showed a singlet of two protons at τ 6.59, a singlet of three protons at τ 6.72 and a signal of three protons centered at τ 6.32 showing a fine splitting (2 Hz). This splitting indicated that **1 c** obtained here is a mixture of two rotamers, as was obtained by ADAM et al. However, **1 b** described above was methylated giving rise to **1 c**, which showed only a three proton singlet at τ 6.33. Accordingly, the original carbomethoxyacetylquercinic acid **1 b**, unlike **1 a**, is stereochemically pure.

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¹ H. INOUE, K. TOKURA, and T. HAYASHI, Tetrahedron Letters [London], **1970**, 2811.

² H. K. ADAM, T. A. BRYCE, I. M. CAMBELL, N. J. MCCORKINDALE, A. GAUDEMER, R. GELIN, and J. POLONSKY, Tetrahedron Letters [London] **1967**, 1461.

** Although our carboxyacetylquercinic acid has not yet been identified with the specimen of ADAM et al., the identity is evident from the comparison of the physical data.

Refluxing **1a** or **1c** with aqueous methanolic KOH yielded quercinic acid **2a** ($\text{C}_{31}\text{H}_{50}\text{O}_4$, mp $217-221^\circ$), which was further converted to the methyl ester **2b**, mp $137-138^\circ$ and the acetate **2c**, mp $243-244^\circ$. Enol lactonization of **2c** with acetic anhydride and sodium acetate afforded two isomeric α , β -unsaturated γ -lactones **3a**, mp $276-279^\circ$, and **3b**, mp $193-195^\circ$, and their double bond isomer **4**, mp $214-216^\circ$. The NMR spectrum of **4** showed a double doublet (J , 1.5, 10 Hz) at τ 5.58 (olefinic proton on C-22). Ozonolysis of **4**, followed by oxidative degradation with Jones' reagent, gave the carboxylic acid **5**, mp $271-273^\circ$. **5** was subjected to hydrolysis followed by methylation and subsequent oxidation with chromium trioxide to give the ketoester, which was converted into **6** $\text{C}_{28}\text{H}_{44}\text{O}_4$, mp $184-185^\circ$ by NaBH_4 reduction and successive acetylation.

On the other hand lanosteryl acetate **7** was converted to **6** in the following way. Ozonolysis of **7** gave rise to

the tricarboxylic acid **8a**, mp $208-212^\circ$, which was methylated to yield **8b**, mp $179-180^\circ$. **8b** was subjected to Grignard reaction with methyl-magnesium iodide and successive acetylation. However, as about one fifth of this reaction product was the $\Delta^{7,9(11)}$ -diene compound, formed during the ozonolysis and Grignard reaction, it was hydrogenated over Pd-C affording the Δ^8 -monoene **9**, mp $172-173^\circ$, as the sole product. This was dehydrated with POCl_3 , successively ozonolysed and methylated to yield **10**, mp $156-159^\circ$. The carbon chain of **10** was contracted by one carbon atom by the same degradative procedures as described above for **8b** to give a compound, mp $184-185^\circ$, which was identified with **6** derived from the enol lactone **4**. The negative Cotton effects observed in the CD curves of **1a**, **1b**, **1c**, **2b** suggest an R-configuration at C-24. As described above, **1a** is a mixture of C-25 epimers, so that the absolute structure of carboxy-acetylquercinic acid was established.