

Selinene IV is the first enantiomeric selinene isolated from a plant source¹⁷, and the third case of liverworts yielding previously unknown enantiomers of sesquiterpenes common in higher plants⁵. This contrasts to the nearly universal presence of 7 β -isopropyl groups in higher plant products¹⁸. Further studies of the more primitive plants should thus reveal the phylogeny of vascular plants and the point in evolution at which this exceptional consistency in absolute configuration¹⁸ developed.

¹⁷ (–)-Germacrene-A and some related selinenes have however been isolated from marine invertebrates: A. J. WEINHEIMER, W. W. YOUNGBLOOD, P. H. WASHECHECK, T. K. B. KARNS and L. S. CIERESZKO, *Tetrahedron Lett.* 1970, 497.

¹⁸ N. H. ANDERSEN, *Phytochemistry* 9, 145 (1970).

¹⁹ N. H. ANDERSEN and D. D. SYRDAL, *Tetrahedron Lett.* 1972, 2455. See ref. ¹⁸ and also N. H. ANDERSEN and D. D. SYRDAL, *Tetrahedron Lett.* 1970, 2277.

Assuming the applicability of the framework of biogenetic conjecture for higher plants¹⁹ (as seems likely due to the general similarities between liverwort and e.g. conifer sesquiterpene oils) the following can be proposed: Clearly intermediate V cannot yield cadalane structure I, the structure proposed for chiloscyphone, suggesting the need for further studies on the configuration of that substance.

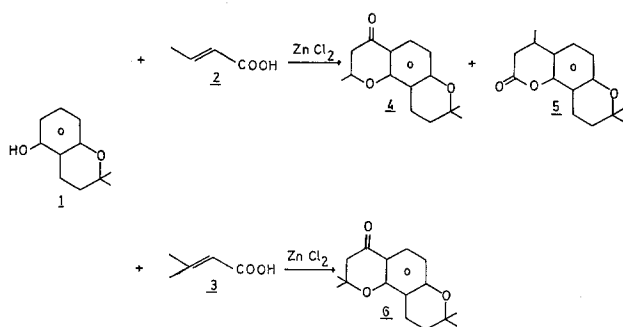
Zusammenfassung. Nachweis des optischen Isomeren eines Sesquiterpens im Lebermoos *Chiloscyphus polyanthus* mit (+)- α -Selinen als Hauptanteil.

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Synthesis of Chromanones from 5-Hydroxy-2,2-Dimethylchroman and α,β -Unsaturated Acids

The acid-catalysed condensation of polyphenols with α,β -unsaturated acids is a valuable synthetic method for the preparation of 4-chromanones^{1,2}. During studies aimed at the synthesis of rotenoids, we investigated the reaction of 5-hydroxy-2,2-dimethylchroman³ with α,β -unsaturated acids in the presence of Friedel-Craft catalysts. 5-Hydroxy-2,2-dimethylchroman (**1**) reacted with crotonic acid (**2**) in the presence of zinc chloride to yield a mixture of two products, 9,10-dihydro-2,8,8-trimethyl-8H-[1]pyrano[2,3-h]chroman-4-one (**4**) and 9,10-dihydro-4,8,8-trimethyl-8H-[1]pyrano[2,3-h]chroman-2-one (**5**) separated by column chromatography. Reaction of the phenol **1** with β,β -dimethylacrylic acid (**3**) afforded only the chroman-4-one compound 9,10-dihydro-2,2,8,8-tetramethyl-8H-[1]pyrano[2,3-h]chroman-4-one (**6**).



Distinction between 2-chromanones and 4-chromanones can be made by IR. The carbonyl frequency falls in the range of 1760–1740 cm^{-1} (lactone) for 2-chromanones, while lower frequencies arise in the 4-chromanones by the effect of conjugation (1680–1650 cm^{-1}). The NMR-spectra showed sharp signals for each gem-dimethyl group in **4**, **5** and **6**. The methylene and methine protons of the chromanone ring appeared as an ABX pattern for compound **4** and as an ABC pattern for compound **5**. One of the aromatic protons of **4** and **6** exhibited a large deshielding effect of ± 0.8 ppm by the anisotropy of the carbonyl function. The most prominent peak in the mass spectrum of **5** arose from a retro-Diels-Alder reaction with

hydrogen shift in the pyrano ring (m/e 191). Another retro-Diels-Alder fragmentation occurred in the chromanone ring affording an ion (m/e 204) of moderately large relative intensity, followed by another retro-Diels-Alder fragmentation (m/e 149 and 148). The minor pathway involved loss from M^+ of a methyl radical and the consecutive expulsions of methyl radicals and CO or vice versa from the ion m/e 204.

Compound **4**: ν_{max} (KBr) 1675 (CO); 1600, 1440 and 815 cm^{-1} (aromatic) δ (CCl_4) 1.31 (3H, s, CH_3); 1.32 (3H, s, CH_3); 1.49 (3H, d, J 6.0 cps, CH_3); 1.75 (2H, t, J 7.2 cps, CH_2); 2.45 (1H, dxd, J 14 cps, J 7 cps, C H); 2.61 (2H, t, J 7.2 cps, CH_2); 4.3–4.6 (1H, m, CH); 6.34 (1H, d, J 9 cps, Ar-H); 7.56 (1H, d, J 9 cps, Ar-H). m/e 246(68) 231(10) 191(100) 149(45) 148(15).

Compound **5**: ν_{max} (KBr) 1760 (CO); 1620, 1440, 830 (aromatic) δ (CCl_4) 1.29 (3H, d, J 6 cps, CH_3); 1.32 (6H, s, $2 \times \text{CH}_3$); 1.76 (2H, t, J 7 cps, CH_2); 2.3–2.6 (2H, m, CH_2); 2.76 (2H, t, J 7 cps, CH_2); 2.9–3.1 (1H, m, CH); 6.42 (1H, d, J 8.1 cps, Ar-H); 6.82 (1H, d, J 8.1 cps, Ar-H); m/e 246(51) 231(50) 204(22) 191(100) 190(30) 175(25) 161(23) 149(75) 148(19).

Compound **6**: ν_{max} (KBr) 1675 (CO); 1595, 1580, 815 cm^{-1} (aromatic) δ (CCl_4) 1.33 (6H, s, $2 \times \text{CH}_3$); 1.44 (6H, s, $2 \times \text{CH}_3$); 1.76 (2H, t, J 6.1 cps, CH_2); 2.52 (2H, s, CH_2); 2.59 (2H, t, J 6.1 cps, CH_2); 6.30 (1H, d, J 9 cps, Ar-H); 7.52 (1H, d, J 9 cps, Ar-H); m/e 260(100) 245(85) 204(30) 189(34) 176(24) 149(64).

Zusammenfassung. Die Synthese von 2- und 4-Chromanonen aus 5-Hydroxy-2,2-dimethylchroman und Crotonsäure oder β,β -Dimethylacrylsäure wird beschrieben.

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¹ M. MIYANO and M. MATSUI, *Chem. Ber.* 91, 397 (1958).

² A. S. R. ANJANEYULI, *Current Sci.* 37, 513 (1969).

³ R. VERHÉ, PhD Thesis, State University of Ghent 1972.