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Synthesis of (±)-Officinalic Acid*

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A new concept for the biosynthesis of officinalic acid (*1*), a C_{30}-metabolite from the fungus *Laricifomes officinalis*, had led to an efficient synthesis of the racemic form of this compound. The key step involves a Diels-Alder dimerization of the readily available enone acid (±)-*3*, which furnishes (±)-officinalic acid in 42% yield. A byproduct formed in the same reaction in 10% yield has been named isoofficinalic acid and shown by spectroscopic techniques to possess structure *11*.

Officinalic acid, $C_{30}H_{44}O_6$, is a constituent of the wood-rotting fungus *Laricifomes officinalis* and is probably identical with a material first isolated by Jahns[1] in 1883 and designated »Harz A«. Structure *1* (without absolute configuration) has been established for officinalic acid by Epstein *et al.*[2] *via* reduction with sodium borohydride to a tetrahydro derivative and X-ray analysis of the corresponding dimethyl ester. The American authors considered officinalic acid as a triterpene of a unique type bearing some similarity to the onoceranes; at the same time they noted that extensive rearrangement of the alleged squalene precursor would be required to give the carbon skeleton of *1*.

The difficulty of providing a rational mechanistic scheme for such a rearrangement coupled with the absence in the structure of officinalic acid (*1*) of biogenetically significant oxygen substituents at C-3, resp. C-3', which are characteristic for genuine triterpenes isolated from the same fungus, *e. g.* dehydroeburicoic acid[3], eburicol[4] and eburicodiol[5], casted some doubts on the triterpenoid nature of officinalic acid and prompted a search for alternative biogenetic schemes.

A striking feature of officinalic acid (*1*) resides in the symmetry of its carbon skeleton and its essential functionalities. When this clue was exploited in a retrobiosynthetic analysis it soon became evident that the enol ether *2* (scheme 1), a likely precursor of *1*, bears all the marks of a compound easily assembled by Diels-Alder dimerization of the C_{15}-unit *3*. According to this perspective officinalic acid should be viewed as a bis-sesquiterpene rather than as a genuine triterpene.***

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* Dedicated to Professor M. Lj. Mihailović on the occasion of his 60th birthday.

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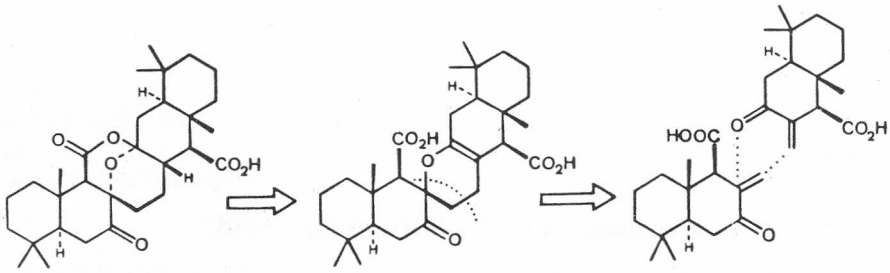
*** A related biogenetic problem is posed by the C_{20}-compound aritasone which can be considered as a dimer of (—)-pinocarvone.[6]

Scheme 1



1 2 3

To substantiate this hypothesis it was decided to investigate the *in vitro* dimerization of the enone acid *3*. An easy access to the racemic form of this compound was gained as follows (*cf.* scheme 2). A mixture containing (±)--drimenine (*4*) and (±)-isodrimenine (*5*) was prepared in 3 steps from monocyclofarnesic acid as described by Kitahara *et al.*[7] and oxydized with Beckmann's mixture to give (±)-*6*, which was subsequently reduced with zinc in acetic acid to (±)-7.

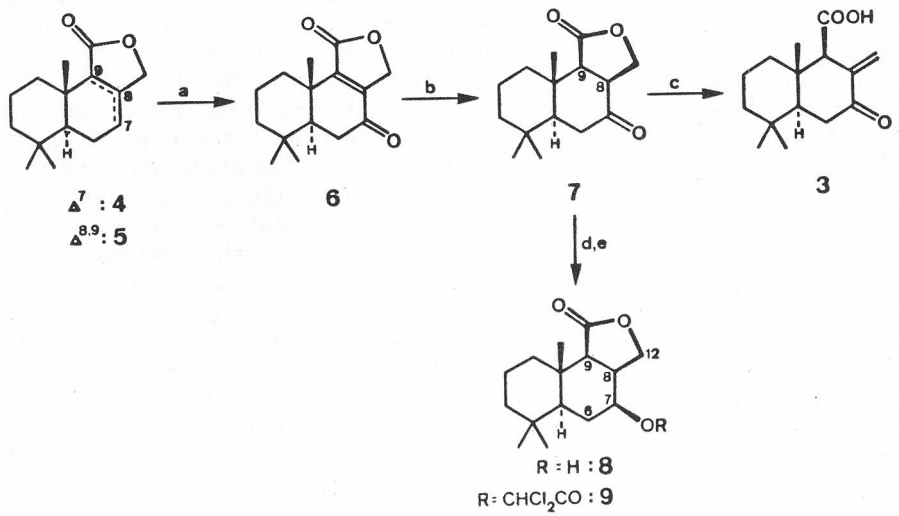
The enantiomerically pure (—)-form of this compound had already been prepared by Overton and coworkers[8] by application of the same procedure to (—)-drimenine. The 8,9-cis stereochemistry suggested for 7 by these authors was later challenged by Brooks and Draffan[9], who favoured a *trans* fusion of the lactone ring on the basis of ^{1}H-NMR arguments. Although the stereochemistry of this ring fusion is irrelevant for the purpose of our synthesis, we attempted to settle the issue through conversion of 7 with sodium borohydride into 8*, which was subsequently transformed into the dichloroacetate *9*. The equatorial nature of the acyloxy group in *9* is well supported by the splitting pattern of the ^{1}H-NMR signal of the corresponding geminal proton which displays a large coupling constant (J = 11.9 Hz) du to a *trans*-diaxial interaction with H_{ax}—C(6). The two additional coupling constants of 6.0 and 7.5 Hz which can be discerned in this signal are incompatible with further *trans*-diaxial H/H-interactions** and can be used as an independent support of the original proposal[8].

Treatment of (±)-7 with DBU in boiling methylene chloride generated a UV-active compound as main product. While all attempts of purification of this compound led to its decomposition, the spectral data of the crude material (*cf.* Experimental) were fully consistent with the presence of the desired enone acid *3* (scheme 2). Thermal treatment of (±)-*3* (boiling toluene, 3 hours) produced a reaction mixture from which a major component could be isolated in 36% yield by crystallization. This material was recognized as racemic

* The (—)-form of this compound, first prepared by Wenkert and Strike[10], has been recognized ever since as a natural product and assigned a *trans*-fused lactone structure.[11]

** The observed values lie slightly outside the range which is normally accepted for ax/eq-interactions and suggest that ring B takes up a distorted chair conformation with C(12) bending outwards; in this conformation the critical dihedral angles for H—C(7)/H—C(8) and H—C(8)/H—C(9) amount to *ca.* 20° and 10°, respectively.

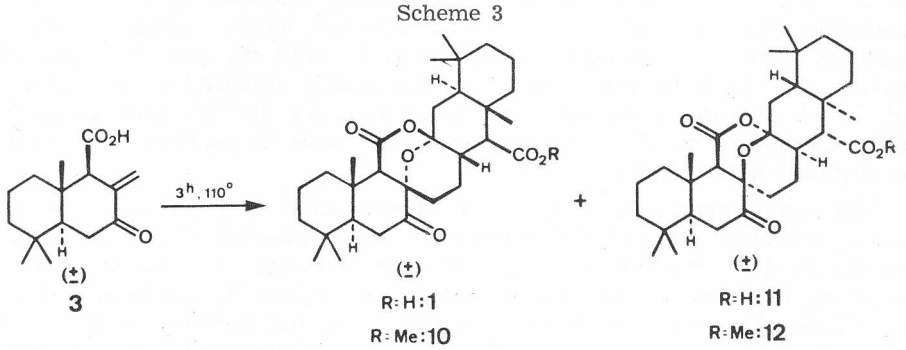
Scheme 2



Reagents: a) $Na_2Cr_2O_7$, H_2SO_4; b) Zn, AcOH; c) DBU, CH_2Cl_2; d) $NaBH_4$; e) $CHCl_2COCl$, pyridine.

officinalic acid ((±)-*1*) by direct comparison with an authentic specimen of (—)-*1*, isolated from *Laricifomes officinalis*. After esterification of the mother liquors with diazomethane two new components were isolated in pure state by liquid chromatography. The less polar one was identified as (±)-methyl officinalate ((±)-*10*, scheme 3) by comparison with the product of esterification of (±)-*1*.* The more polar component was recognized from its spectral data (*cf.* below) as a stereoisomer of (±)-*10* and named, accordingly, methyl iso-officinalate.

Scheme 3



* Whereas the ^{1}H-NMR spectrum of (±)-*10* coincides well with the one of an authentic specimen of (—)-*10*, prepared from natural (—)-officinalic acid with CH_2N_2, these two spectra lack in the low-field region the two 2H-singlets at 3.24 and 2.49 ppm recorded by Epstein *et al.*[2] for their preparation of (—)-*10*, which therefore most probably reflect the presence of unidentified impurities in their sample.

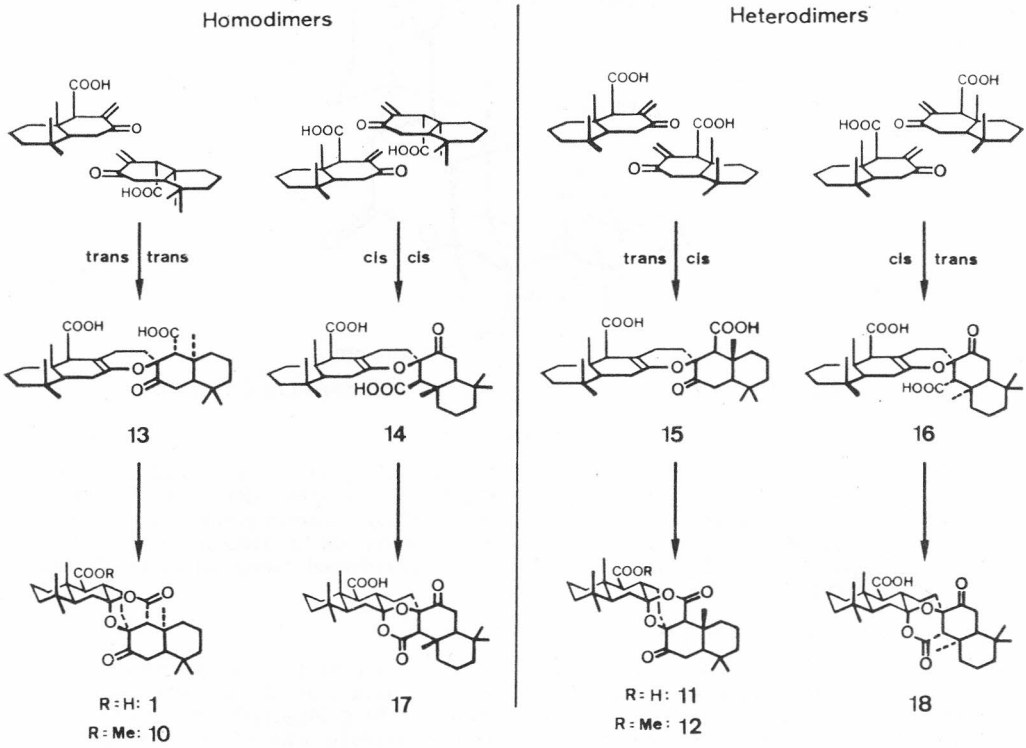
Before discussing the stereochemistry of isoofficinalic acid it is necessary to analyze in detail the relevant factors which govern the outcome of the dimerization process (for an exhaustive discussion of a related case see[12]). These are a) the homo- *vs.* heterochiral relationship of the monomeric partners involved, b) the *trans- vs. cis*-mode of addition with respect to the angular methyl group of the oxadiene component and c) the *trans- vs. cis*-mode of addition with respect to the angular methyl group of the dienophile. Within each of the a)-sets a given combination of the last two factors determines whether the addition is occuring as an *endo*- or as an *exo*-process. In scheme 4 only the four combinations corresponding to *endo*-additions have been considered. In principle, of course, each of the resulting four stereoisomers *13*—*16** can also be generated through an *exo*-addition process; however, these four alternatives have been dismissed from further consideration because they do not cast additional light on the combinatory problem discussed inhere and because the *endo*-mode of addition can be taken *a priori* as more favourable both on electronic and on steric accounts. As for the ensuing lactonization step we have restricted our attention in each case to those processes which generate thermodynamically favoured structures containing exclusively chair forms of all the rings, as is the case in officinalic acid itself[2].

On this basis we can now return to a consideration of the stereochemistry of methyl isoofficinalate. In the ^{1}H-NMR spectrum of this compound a well-separated, complex signal at 2.30 ppm can be assigned with confidence to the C(8')-proton on the basis of decoupling experiments disclosing a correlation with a characteristic doublet at 2.44 ppm (J = 12.7 Hz) which can only be assigned to H—C(9'). The values of the residual coupling constants (J = 4.7 and $\leq$ 2 Hz) in the signal at 2.30 ppm insure that the C(8')-proton is equatorially arranged with respect to the tetrahydropyrane ring to which it is attached (*cf.* Figure 1). Within the set of the stereoisomers *1, 11, 17* and *18* this structural feature is present only in officinalic acid (*1*) and in isomer *11*; the latter must therefore represent the correct structure of isoofficinalic acid. In accord with the axial arrangement of the ether bond α to the keto group required by structure *11* a batho- and hyperchromic shift of the n—π^*--transition ($\Delta\lambda$ = 10 nm, $\Delta\varepsilon$ = 13) was detected when comparing the UV spectrum of the corresponding methyl ester *12* with the one of methyl officinalate (*10*). In turn, the presence of an axially oriented oxygen atom at C(8) in *12* provides a satisfactory explanation for the 0.3 ppm down-field shift experienced by H_{ax}—C(6) in comparison with its position in *10* and in the drimane derivatives *3*—*9*.

The experimental outcome of the dimerization of (±)-*3* deserves some further comment: although the presence of small amounts of *17* and *18* in the reaction mixture can not be ruled out with certainty, it is noteworthy that out of the four possible stereoisomers only two (*1* and *11*) are formed in sizeable yields. The observed 4 : 1-predominance of the homodimer *1* over the heterodimer *11* is in accord with the findings of Eschenmoser and coworkers

* Structures *13* and *14* have been considered by Overton and coworkers[8] for a product of the thermal decomposition of (+)-12-ethoxy-7-oxodrimane-11-carboxylic acid. Our results suggest that the English authors actually had a slightly impure sample of optically active officinalic acid (*1*) in their hands.

Scheme 4 *



* Although all compounds in this scheme are racemic, only one enantiomer of each is shown. For convenience, the same absolute configuration was chosen in all 4 cases for the monomer which acts as oxadiene unit.

for a similar system[12] and can be explained through an inspection of the transition states leading to *13—16* (*cf.* scheme 4) which reveals that only in the *endo-trans-trans* addition mode all axial substituents are located on the convex side of the collision complex between two monomers. The fact that isoofficinalic acid, the only stereoisomer detected as a byproduct of *1* in the dimerization process, is built from heterochiral monomeric partners bodes well for the specific outcome of a thermal dimerization process involving enantiomerically pure forms of the monomeric unit *3*.

While the biogenetic considerations which initiated this project have paved the way for an efficient synthesis of (±)-officinalic acid, a relatively complex structure containing 9 asymmetric centres, it is felt that the remarkable ease with which (±)-*3* dimerizes to (±)-*1* can be taken, in turn, as an indirect, but nevertheless compelling argument in support of the biogenetic proposal presented in scheme 1.

Acknowledgment. — Financial support from SANDOZ AG, Basel, is gratefully acknowledged.

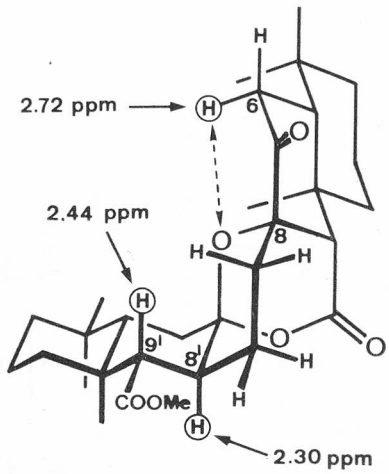


Figure 1. A stereorepresentation of methyl isoofficinalate (*12*).

EXPERIMENTAL

Melting points (m. p.) are uncorrected. The IR spectra were recorded on a Perkin-Elmer 297 spectrometer. The ^{1}H-NMR spectra (300 MHz) and ^{13}C-NMR spectra (75.4 MHz) were run with a Bruker WM-300 spectrometer with TMS as internal standard. The mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6M aparatus. Flash chromatography[13] was performed using silica 60 (Merck, 0.04—0.063 mm).

(±)-7-Oxo-isodrimenine (6)

To a solution of a 6 : 1-mixture of racemic drimenine (*4*) and isodrimenine (*5*), prepared according to Kitahara *et al.*[7], (49 mg, 0.18 mmol) in 2.5 ml acetic acid were added 0.5 ml of a solution prepared by dissolving 10 g $Na_2Cr_2O_7$ in a mixture of 8.7 g H_2SO_4 and 50 ml of water. The resulting mixture was stirred overnight at room temperature, poured onto ice and extracted with 3 portions of ether. The organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. The crude product was chromatographed (hexane : ethyl acetate, 5 : 1) to yield 23 mg (49%) of (±)-*6*, which was crystallized from ether : hexane. M. p. 107—108 °C. Lit.[8] m. p. 112—113 °C for optically active material.

Anal. $C_{15}H_{20}O_3$ (248.3) calc'd.: C 72.55, H 8.12%
found: C 72.48, H 8.07%

(±)-Dihydro-7-oxo-isodrimenine (7)

To a solution of (±)-*6* (1.10 g, 4.44 mmol) in 60 ml of acetic acid were added 5.5 g of zinc dust in portions. The resulting suspension was heated at reflux for 2 hours, allowed to cool, filtered and evaporated. The ether-soluble part of the residue was chromatographed (hexane : ethyl acetate, 3 : 1) to give 800 mg (72% yield) of pure (±)-*7*, which was crystallized from ether : hexane.

M. p. 99—101 °C. Lit.[8]: 124—126 °C for an optically active specimen.

Anal. $C_{15}H_{22}O_3$ (250.3) calc'd.: C 71.96, H 8.86%
found: C 71.90, H 8.74%

(1RS,4aSR,8aSR)-2-Methylidene-3-oxo-5,5,8a-trimethyldecahydro--1-naphtoic acid (3)

To a solution of lactone 7 (31 mg, 0.124 mmol) in 20 ml of dry CH_2Cl_2 were added 150 mg (0.99 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Fluka, purum).

The resulting solution was stirred at 40 °C for 2.5 hours. The mixture was poured onto ice and extracted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4) and evaporated to give 32 mg of a white foam, which according to TLC and ^{1}H-NMR spectrum consisted of at least 70% (±)-*3*. Since all attempts to purify this material resulted in its decomposition, enone *3* was characterized in this crude state.

IR ($CHCl_3$): 1748(m, sh), 1710(s), 1695(s), 1608(m), 1467(m), 1392(m).
UV spectrum: $\lambda_{max} = 231$ nm, $\log \varepsilon \geq 3.54$ (ethanol).

^{1}H-NMR spectrum ($CDCl_3$): 8.7 (br. s, 1H), 6.19 (d, $J = 2.4$, 1H), 5.32 (d, $J = 2.4$, 1H), 3.22 (t, $J = 2.4$, 1H), 2.63 (dd, $J = 18.4$ and 4.9, 1H), 2.39 (dd, $J = 18.4$ and 13.6, 1H), 1.57 (dd, $J = 13.6$ and 4.9, 1H), 1.12 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H).

^{13}C-NMR spectrum ($CDCl_3$): 200.3(s), 175.9(s), 140.8(s), 123.3(t), 61.6(d), 50.6(d), 41.3(t), 38.6(t), 37.6(s), 37.5(t), 33.4(s), 32.5(q), 20.9(q), 18.5(t), 14.1(q). Mass spectrum: 250 (M^+, 0.6), 194(3), 123(8), 122(8), 86(39), 84(100), 69(16), 57(17), 41(16).

Dimerization of racemic enone 3

A solution of crude *3* (161 mg, 0.64 mmol) prepared as above, in 1.5 ml of toluene was heated at reflux for 3.5 hours. Then the solvent was removed under reduced pressure and the residue was crystallized from CH_2Cl_2: acetone : hexane to give pure racemic officinalic acid (*1*) (59 mg, 36% yield). M. p. 235—237 °C, dec. Lit.[2] 272 °C for natural (—)-*1*. The spectral data (IR, ^{1}H-NMR, ^{13}C-NMR, mass spectrum) of our synthetic (±)-*1* were indistinguishable from the values obtained for a sample of authentic (—)-*1*, isolated from *Laricifomes officinalis*.

The mother liquor was dissolved in CH_2Cl_2 and treated with a slight excess of etheral diazomethane. Chromatography (toluene : ethyl acetate, 25 : 1) gave 10 mg (6% yield) of racemic methyl officinalate (*10*) after crystallization from ether : hexane and 16 mg (10% yield) of methyl isoofficinalate (*12*), which was crystallized from acetone : hexane.

Characterization of (±)-methyl officinalate (10)

M. p. 210—211 °C.

UV spectrum: $\lambda_{max} = 289$ ($\varepsilon = 35$) (CH_2Cl_2).

IR spectrum ($CHCl_3$): 1733(s), 1392(m), 1371(m), 1295(m), 1175(s), 1083(m), 1051(m).

^{1}H-NMR spectrum ($CDCl_3$): 3.61(s, 3H), 2.83(m, 1H), 2.52 (d, $J = 12.6$, 1H), 2.48 (m, 2H), 2.45 (s, 1H), 2.34 (br. dd, $J = 12.6$ and 4.1, 1H), 2.16 (ddd, $J = 13.0$, 4.0 and 2.6, 1H), 2.07 (m, 1H), 1.97 (dd, $J = 13.3$ and 2.9, 1H), 1.80 (t, $J = 13.3$, 1H), 1.79 (ddd, $J = 13.3$, 13.0 and 4.9, 1H), 1.69 (m, 1H), 1.48 (dd, $J = 13.3$ and 2.8, 1H), 1.31 (s, 3H), 1.06 (s, 3H), 0.90 (s, 3H), 0.87 (s, 3H), 0.85 (s, 3H), 0.83 (s, 3H).

^{1}H-NMR spectrum (C_6D_6): 3.36 (s, 3H), 3.00 (m, 1H), 2.69 (d, $J = 12.6$, 1H), 2.42 (ddd, $J = 12.6$, 5.2 and 1.5, 1H), 2.23 (s, 1H), 2.21 (dd, $J = 13.7$ and 2.5, 1H), 2.15 (dd, $J = 13.3$ and 2.6, 1H), 2.05 (m, 2H), 1.98 (dd, $J = 14.4$ and 13.7, 1H), 1.86 (dd, $J = 13.4$ and 13.2, 1H), 1.66 (dd, $J = 13.4$ and 2.6, 1H), 1.07 (s, 3H), 1.06 (s, 3H), 0.92 (s, 3H), 0.77 (dd, $J = 14.4$ and 2.5, 1H), 0.70 (s, 3H), 0.62 (s, 3H), 0.56 (s, 3H).

^{13}C-NMR spectrum ($CDCl_3$): 205.1(s), 172.8(s), 168.7(s), 106.4(s), 81.1(s), 60.3(d), 56.2(d), 55.4(d), 51.1(q), 48.9(d), 41.5(t), 41.2(t), 39.6(t), 38.9(t), 38.0(s), 37.4(s), 36.2(d), 35.9(t), 34.0(s), 33.8(t), 33.1(q), 32.9(s), 32.8(q), 26.1(t), 21.6(q), 20.7(q), 19.2(t), 18.5(t), 18.1(t), 15.0(q), 13.7(q).

Mass spectrum: 514(M^+, 4), 470(9), 438(21), 252(40), 220(29), 210(100), 135(12), 123(43), 109(24), 69(57).

Characterization of methyl isoofficinalate (12)

M. p. 250 °C.

UV spectrum: $\lambda_{max} = 229$ ($\varepsilon = 49$) (CH_2Cl_2).

IR spectrum ($CHCl_3$): 2935(s), 2875(s), 1730(s), 1460(m), 1395(m), 1372(m), 1300(m), 1178(s), 992(m), 911(m).

^{1}H-NMR spectrum ($CDCl_3$): 3.64 (s, 3H), 2.72 (dd, $J = 14.7$ and 14.3, 1H), 2.47 (dd, $J = 14.7$ and 3.0, 1H), 2.46 (m, 1H), 2.44 (d, $J = 12.7$, 1H), 2.30 (br. dd, $J = 12.7$ and

4.7, 1H), 2.18 (s, 1H), 2.16 (m, 1H), 1.95 (m, 1H), 1.92 (dd, $J = 13$ and 3, 1H), 1.81 (t, $J = 13$, 1H), 1.19 (s, 3H), 1.05 (s, 3H), 0.92 (s, 6H), 0.86 (s, 3H), 0.84 (s, 3H).

^{13}C-NMR spectrum ($CDCl_3$): 204.7(s), 172.7(s), 168.0(s), 105.9(s), 77.3(s), 60.2(d), 56.0(d), 51.7(d), 51.1(q), 48.9(d), 41.3(t), 41.2(t), 40.2(t), 39.1(s), 39.0(t), 37.7(s), 35.9(d), 35.4(t), 34.1(s), 33.7(t), 32.9(2q), 32.8(s), 24.7(t), 21.5(2q), 18.5(t), 18.1(t), 17.6(t), 16.7(q), 13.7(q).
Mass spectrum: 514 ($M^{+\cdot}$, 8), 470(9), 438(18), 349(11), 262(29), 252(72), 219(100), 123(28), 109(25), 69(46).

(±)-7β-Dichloroacetoxydihydrodrimenine (9)

To a slight excess of dichloroacetyl chloride (Fluka, purum) in 5 ml of CH_2Cl_2 containing 0.5 ml pyridine were added 15 mg (±)-7β-hydroxydihydrodrimenine (*8*) which was prepared from (±)-7 by reduction with $NaBH_4$ according to Wenkert and Strike[10]. After 16^h at room temperature the mixture was poured onto ice and extracted with 3 portions of ether. These were washed with cold 0.2 M aq. HCl and then with brine. The organic layers were dried (Na_2SO_4), evaporated and chromatographed (ether : hexane, 2 : 3) to give 20 mg of dichloroacetate *9*, m. p. 136—138 °C, dec., which was characterized by ^{1}H-NMR spectroscopy only.

^{1}H-NMR spectrum ($CDCl_3$): 5.25 (ddd, $J = 11.9$, 7.5 and 6.0, 1H), 4.25 (m, 2H), 2.34 (d, $J = 8.6$, 1H), 1.98 (br. dd, $J = 13.0$ and 6.0, 1H), 1.65 (ddd, $J = 13.0$, 12.5 and 11.9 1H), 1.10 (s, 3H), 1.04 (dd, $J = 12.5$ and 1.6, 1H), 0.95 (s, 3H), 0.90 (s, 3H).

^{1}H-NMR spectrum (C_6D_6): 4.72 (ddd, $J = 11.9$, 7.6 and 6.0, 1H), 3.85 (dd, $J = 9.2$ and 9.0, 1H), 3.78 (dd, $J = 11.5$ and 9.2, 1H), 2.37 (m, 1H), 2.22 (m, 1H), 1.68 (d, $J = 8.6$), 1.55 (br. dd, $J = 12.6$ and 6.0, 1H), 0.78 (s, 3H), 0.62 (s, 3H), 0.54 (s, 3H), 0.35 (dd, $J = 12.4$ and 1.5, 1H).

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IZVOD

Sinteza (±)-oficinalne kiseline

Bernhard Erb, Hans-Jürg Borschberg i Duilio Arigoni

Nov koncept biosinteze oficinalne kiseline (*1*), jednog C_{30}-metabolita gljive *Laricifomes officinalis*, doveo je do efikasne sinteze racemskog oblika ovog jedinjenja. Ključna faza je Diels-Alder-ova dimerizacija lako pristupačne enonske kiseline (±)-*3*, koja daje (±)-oficinalnu kiselinu u prinosu od 42%. Sporedan proizvod nagrađen pri istoj reakciji u prinosu od 10% nazvan je izo-oficinalna kiselina, a spektroskopski podaci pokazuju da poseduju strukturu *11*.