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epi-Cubebanes from *Solidago canadensis*

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Abstract

GC–MS of the essential oil prepared by hydrodistillation of the green parts of a specimen of *Solidago canadensis* collected near Katowice, Poland, revealed two new sesquiterpene hydrocarbons. Their EI mass spectra resembled the mass spectrum of β-ylangene (**1**) but the retention indices of the new compounds differed markedly from this known compound. After isolation of the new compounds by preparative GC their investigation by one- and two-dimensional NMR techniques resulted in the identification of 6-*epi*-α-cubebene (**2**) (minor constituent, 1.5%) and 6-*epi*-β-cubebene (**3**) (major constituent, 20.5%).

Keywords: *Solidago canadensis*; Essential oil; Structure elucidation; Cubebane; Sesquiterpene

1. Introduction

The essential oils of several *Solidago* species have been investigated before (Kalemba et al., 2001; Bülow and König, 2000; Weyerstahl et al., 1993; Niwa et al., 1980). In most cases germacrene D was found to be the predominant constituent in *Solidago* species and the occurrence of both enantiomers of this sesquiterpene hydrocarbon has attracted particular interest (Niwa et al., 1980; Schmidt et al., 1998; Bülow and König, 2000). In this investigation of the green parts of a specimen of *Solidago canadensis* collected near Katowice, Poland, (−)-germacrene D was also identified as the main constituent, however, another abundant sesquiterpene hydrocarbon with a mass spectrum with $m/z = 120$ as base peak very similar to β-ylangene (**1**) (Joulain and König, 1998), but with a different retention index, was detected by GC–MS of the essential oil. In addition, another minor component, also with a mass spectrum very similar to β-ylangene but again with a different retention index was found in this sample. After the isolation of the new compounds by preparative GC their investigation by one- and two-dimensional NMR techniques resulted in the identification of the minor component as 6-*epi*-α-cubebene (**2**) and the major component as 6-*epi*-β-cubebene (**3**).

2. Results and discussion

The analysis of the essential oil of *Solidago canadensis* by GC and GC–MS allowed the identification of (relative concentrations given in parentheses) *trans*-2-hexenol (0.3%), α-pinene (2.9%), camphene (0.4%), β-pinene (0.5%), myrcene (5.1%), limonene (2.7%), bornyl acetate (1.8%), α-copaene (1.2%), β-elemene (1.4%), β-caryophyllene (1.5%), α-humulene (0.3%), germacrene D (23.8%), β-selinene (0.5%), bicyclogermacrene (5.0%), δ-amorphene (**5**) (0.9%) (Melching et al., 1997), γ-cadinene (4.1%), δ-cadinene (0.4%), α-cadinene (0.6%), gemacrene B (6.3%), 6-*epi*-cubenol (**4**) (2.9%) by comparison with a spectral library established under identical experimental conditions (Joulain and König, 1998). However, two compounds **2** (1.5%) and **3** (20.5%) could not be identified by their mass spectra and retention times and were isolated for NMR investigation.

From the molecular ion signal at m/z 204 of **2** the elemental composition of $C_{15}H_{24}$ can be concluded. This finding was confirmed by the ^{13}C NMR/PENDANT technique, which showed four primary (δ 16.86, 20.19, 21.08, 21.12), three secondary (δ 23.99, 32.98, 40.53), six tertiary (δ 31.88, 33.85, 35.28, 35.86, 41.16, 120.73), and two quaternary carbons (δ 32.73, 145.20). From these data the presence of one double bond is derived. As the elemental composition of $C_{15}H_{24}$ indicates 4 unsaturations a tricyclic ring system in addition to the double bond must be present. The ^1H NMR of **2**

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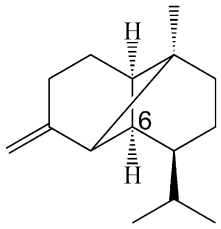
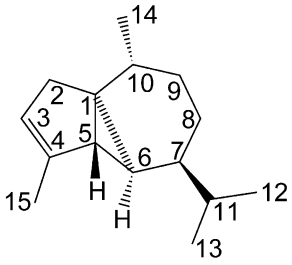
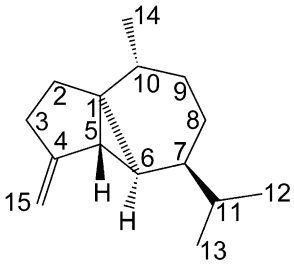


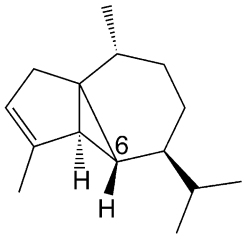
β-Ylangene (**1**)



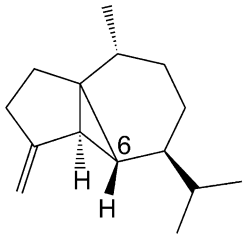
6-*epi*-α-Cubebene (**2**)



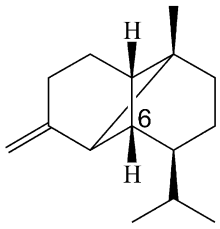
6-*epi*-β-Cubebene (**3**)



α-Cubebene (**7**)



β-Cubebene (**8**)



β-Copaene (**9**)

shows three methyl doublets in the region of $\delta = 0.9$–1.1 (H-12, H-13, H-14) and one down-field shifted methyl signal at $\delta = 1.79$ (H-15). The absorption of one olefinic proton is detected $\delta =$ at 4.98 (H-3). Two cyclopropane protons show resonances at $\delta = 0.55$–0.59 (H-6) and 1.26–1.30 (H-5). Two unusually high-field shifted proton signals as parts of methylene groups appear at $\delta = 0.64$–0.72 (H-8a) and at 0.89–1.04 (H-9a). This high-field shift of signals is attributed to the fact that the protons must be in the anisotropic range of the cyclopropane ring system. The two methylene protons are parts of adjacent methylene groups as revealed by $^1H^1H$-COSY (Table 1). The other protons of each methylene group appear in the aliphatic region of the spectrum: H-8b is located in a multiplet together with two methine protons (δ 1.37–1.46 H-7/H-8b/H-11), H-9b is absorbing at $\delta = 1.46$–1.53. Two protons (H-2a, H-2b) belonging to one methylene group appear as multiplets at $\delta = 2.26$–2.35

Table 1
Two-dimensional NMR correlations of 6-*epi*-α-cubebene **(2)**

Proton and / or carbon	$^1H^1H$-COSY-couplings	HMBC-couplings
C-1 / C-9	–	H-2b, H-3, H-6, H-9b, H-10, H-14
H-2a / C-2	H-2b, H-5, H-15	H-3, H-6
H-2b	H-2a, H-3, H-15	–
H-3 / C-3	H-2a, H-2b, H-15	H-2b, H-5, H-15
C-4	–	H-2b, H-6, H-15
H-5 / C-5	H-2a, H-6	H-3, H-15
H-6 / C-6	H-5, H-7/H-8b/H-11	H-7/H-8b/H-11, H-8a
H-7/H-8b/H-11	H-6, H-12, H-13	–
C-7	–	H-5, H-7/H-8b/H-11, H-8a, H-9b, H-12, H-13
H-8a / C-8	H-9a, H-9b	H-6, H-7/H-8b/H-11, H-9b
H-9a	H-8a, H-9b, H-10, H-14	–
H-9b	H-8a, H-9a	–
H-10 / C-10	H-9a, H-9b, H-14	H-5, H-9b
C-11	–	H-7/H-8b/H-11, H-8a, H-12, H-13
H-12 / C-12/C-13	H-7/H-8b/H-11	H-7/H-8b/H-11, H-12, H-13,
H-13	H-7/H-8b/H-11	–
H-14 / C-14	H-9a, H-10	H-9b, H-10
H-15 / C-15	H-2a, H-2b, H-3	–

and 2.62–2.70, respectively. The down-field shifted methyl signal, which is split into a dd with $J_1 = 2$ Hz and $J_2 = 4$ Hz can be rationalised as one ^4J coupling to the olefinic proton (2 Hz) and the other as ^5J homoallylic scalar coupling in this rigid system with one of the protons H-2a or 2b. The corresponding crosspeaks appear in the ^{1}H^{1}H-COSY (Table 1). The connectivity of the different groups was established through two-dimensional NMR experiments. The ^{1}H^{1}H-COSY revealed the presence of an isopropyl group due to identical cross peaks to the multiplet of H-7/H-8b/H-11. This finding was further confirmed by the HMBC in which carbon C-11 couples to both methyl doublets H-12 and H-13. The same applies to carbon C-7, which also couples to both methyl doublets (H-12, H-13) and additionally to H-5, H-8a and H-9b. As H-9a couples to the methine proton H-10 and the methyl doublet H-14, the connectivities in the six-membered ring are established. The adjacent quaternary carbon C-1 reveals correlations to H-2b, H-3, H-6, H-9b, H-10 and H-14, which is consistent with the cubebane sesquiterpene skeleton.

The relative configuration of **2** was established through NOE experiments. Proton H-5 shows dipolar couplings to H-10, H-9a, H-8a and H-13 (Fig. 1). Consequently, all these protons have to be in one plane. The lack of dipolar correlation between H-5 and H-6 indicates a *trans* configuration of these two protons. Additionally, H-6 doesn't show cross peaks with the methylene or the methine proton correlating with H-5. Methyl group H-14, which is attached to C-10, shows close spatial relationship to both protons at carbon C-2. This can only be rationalised if this methyl group is in equatorial and

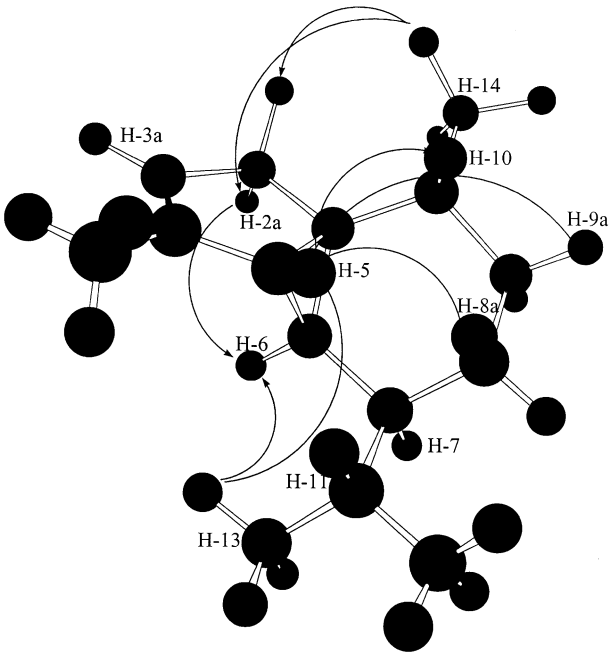


Fig. 1. Observed important NOE couplings for compound **2**. (Couplings of other protons omitted for clarity.)

H-10 in axial position. One of the protons in 2-position, H-2a, shows a correlation to H-6, which itself couples to H-13. As the trans-oriented cyclopropane protons H-5 and H-6 both couple to the methyl group H-13 the isopropyl group must be equatorial.

The elemental composition of $C_{15}H_{24}$ for **3** was calculated from the molecular ion signal at m/z 204. Fifteen carbon atoms showed resonances in the ^{13}C/HMQC and were assigned as three primary (δ 19.94, 20.86, 20.89), five secondary (δ 23.52, 29.16, 31.17, 32.94, 101.46,), five tertiary (δ 27.49, 31.34, 33.44, 33.93, 40.72) and two quaternary carbons (δ 36.00, 154.47). In the ^{1}H NMR two olefinic protons (H-15a: $\delta = 4.80$; H-15b: $\delta = 4.99$) are visible, which belong to one methylene group. Considering this fact together with the ^{13}C data only one double bond is accounted for in this tricyclic system as indicated by the elementary composition $C_{15}H_{24}$.

The ^{1}H NMR shows three methyl signals that are represented by two doublets: one of which integrates to six protons (δ 0.91, H-13, $\delta = 1.01$, H-12, H-14). Again the presence of two up-field shifted methylene protons H-8a (δ 0.63–0.72) and H-9a (δ 0.80–0.90) is noticed. The cyclopropane protons H-6 (δ 1.08–1.12) and H-5 (in a multiplet with H-9b at δ 1.44–1.49) do not appear as much up-field shifted as expected for ordinary cyclopropane protons. This may be caused by the neighbouring double bond. The close proximity of the double bond to the cyclopropane ring is revealed through scalar coupling of H-15a to H-5/H-9b and even to H-6 (^5J homoallylic). H-15b in turn couples to H-5/H-9b (Table 2). These olefinic methylene protons H-15a and H-15b reveal additional scalar couplings to H-2a (δ 1.63), H-3a (δ 1.86–1.96), and H-3b (δ 2.05) in the ^{1}H^{1}H-COSY.

The six-membered ring is established through couplings detected in the HMBC: Carbon C-1 shows correlations equivalent to those observed for compound **2**. The isopropyl group again is established through the couplings of C-7 and of C-9/C-11 to both methyl groups (H-12, H-13). Methyl group H-14 (appearing as one doublet with H-12) gives one signal in the ^{1}H^{1}H-COSY with the multiplet of proton H-2b/H-10 (δ 1.73–1.82). This connection is confirmed by the coupling of C-14 to the same multiplet H-2b/H-10 and to H-9a. The two methylene groups H-8a,b and H-9a,b show scalar couplings in the ^{1}H^{1}H-COSY, by which they were identified as adjacent. Carbon C-8 reveals more information: it indicates a $^3J_{CH}$ coupling with H-6. From this information the connectivity of compound **3** was deduced.

The NOE revealed the *epi*-cubebene structure as depicted in Fig. 2. However, H-6 couples to H-2a, H-3a and H-13 through space. Proton H-9a shows close proximity to both neighbouring groups H-10 and H-14. H-14 itself shows dipolar coupling to H-2a. From this the same relative stereochemistry as in compound **2** is deduced. This was further corroborated by acid catalysed rearrangement of **3** and **2**. The reaction products

Table 2
Two-dimensional NMR correlations of 6-*epi*-β-cubebene **(3)**

Proton and/or carbon	$^1H^1H$-COSY-couplings	HMBC-couplings
C-1	–	H-2a, H-2b/H-10, H-3b, H-5/H-9b, H-9a, H-12/H-14
H-2a/C-2/C-10	H-2b, H-3a, H-3b	H-2a, H-2b/H-10, H-3a, H-3b, H-5/H-9b, H-6, H-7/H-8b/H-11, H-8a, H-9a, H-12/H-14
H-2b/H-10	H-2a, H-3a, H-3b, H-5/H-9b, H-6, H-9a, H-12/H-14	–
H-3a/C-3	H-2a, H-3a, H-2b/H-10, H-5/H-9b	H-2a, H-2b/H-10, H-5/H-9b, H-15a, H-15b
H-3b	H-2a, H-3a, H-2b/H-10, H-5/H-9b	–
C-4	–	H-2a, H-3a, H-3b, H-5/H-9b, H-6
H-5/H-9b/C-5	H-2b/H-10, H-3a, H-3b, H-6, H-8a, H-9a,	H-2a, H-2b/H-10, H-3b, H-6, H-15a, H-15b
H-6 / C-6	H-5/H-9b, H-7/H-8b/H-11	H-2a, H-2b/H-10, H-5/H-9b, H-7/H-8b/H-11, H-8a
H-7/H-8b/H-11	H-6, H-8a, H-9a, H-12/H-14, H-13	–
C-7	–	H-5/H-9b, H-7/H-8b/H-11, H-8a, H-9a, H-12/H-14, H-13
H-8a/C-8	H-5/H-9b, H-7/H-8b/H-11, H-9a	H-2b/H-10, H-5/H-9b, H-6, H-7/H-8b/H-11, H-9a
H-9a / C-9/C-11	H-2b/H-10, H-5/H-9b, H-7/H-8b/H-11, H-8a	H-2b/H-10, H-7/H-8b/H-11, H-8a, H-12/H-14, H-13
H-12/H-14/C-12/C-13	H-2b/H-10, H-7/H-8b/H-11, H-13	H-7/H-8b/H-11, H-12/H-14, H-13,
H-13	H-7/H-8b/H-11, H-12/H-14	–
C-14	–	H-2b/H-10, H-5/H-9b, H-9a
H-15a/C-15	H-2a, H-3a, H-3b, H-5/H-9b, H-6, H-15b	H-3a, H-3b, H-5/H-9b
H-15b	H-2a, H-3a, H-3b, H-5/H-9b, H-15a	–

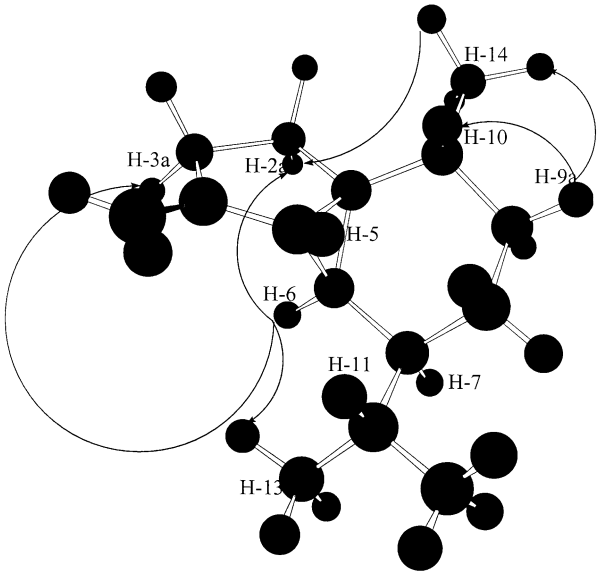


Fig. 2. Observed important NOE couplings for compound **3**. (Couplings of other protons omitted for clarity.)

on treatment with acidic ion exchange resin were in each case (+)-δ-amorphene (**5**) and (+)-6-*epi*-cubenol (**4**). As dehydration of (+)-**4** yielded (−)-*trans*-calamenene (**6**) among other products, the absolute configuration of **2**, **3** and **5** was established as shown in Fig. 3.

It is quite remarkable that the mass spectra of both new compounds are practically undistinguishable from that of β-ylangene (**1**) and totally different from the mass spectra of α- and β-cubebene (**7** and **8**) (Joulain and König, 1998). This again shows that one should be very cautious in identifying unknown compounds only by mass spectral library search. Apparently β-orientation of the hydrogen in position 6 in **1**, **2** and **3** results in a common intermediate after primary ionization and identical or very similar secondary fragmentation in the mass spectrometer. The occurrence of **2** and **3** in *S. canadensis* has never before been reported. Interestingly, in addition to β-ylangene (**1**) and β-copaene (**9**), **3** was obtained as a minor product by irradiation of germacrene D at 254 nm (Bülow and König, 2000).

3. Experimental

3.1. General experimental procedures

3.1.1. Gas chromatography

Orion Micromat 412 double column instrument with 25 m fused silica capillaries with polysiloxane CPSil-5 and polysiloxane CPSil-19 (Chrompack); Carlo Erba Fractovap 2150 or 4160 gas chromatographs with 25 m fused silica capillaries with octakis(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin, heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin or heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin in OV 1701 (50%, w/w), split injection; split ratio approx. 1:30; FID; carrier gas 0.5 bar H_2; injector and detector temperatures 200 and 250 °C, respectively.

3.1.2. Preparative GC

Modified Varian 1400 and 2800 instrument, equipped with a stainless steel column (1.85 m×4.3 mm) with 10% polydimethylsiloxane SE-30 on Chromosorb W-HP or with 6% heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin in SE-52 (50%, w/w) on Chromosorb W-HP; FID; helium as carrier gas at a flow rate

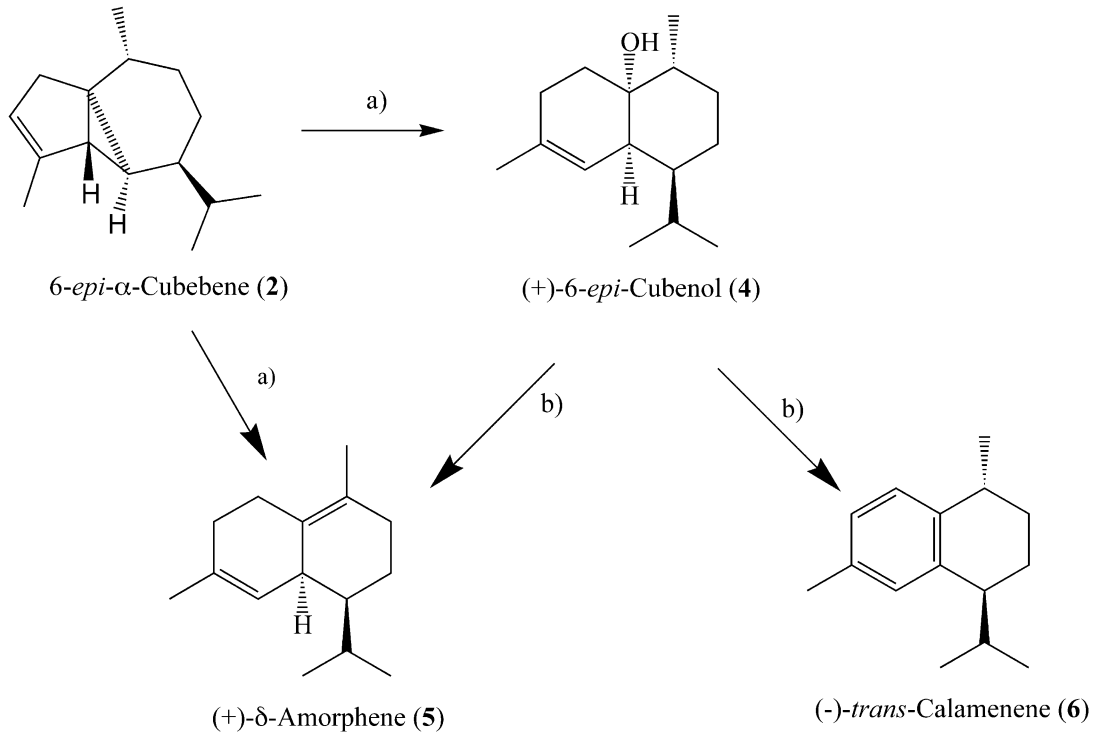


Fig. 3. Reactions performed to elucidate the absolute configuration of the *epi*-cubebenes **2** and **3**. [Reaction conditions: (a) Amberlyst®, benzene, room temperature, 30 min; (b) $SOCl_2$, pyridine/$CHCl_3$ (1:1), 0 °C, 40 min.]

of 240 ml/min; injector and detector temperatures were 200 °C and 250 °C, respectively.

3.1.3. GC–MS

GC–MS measurements (EI, 70 eV) were carried out with a Hewlett Packard HP 5890 gas chromatograph coupled to a VG Analytical 70–250S mass spectrometer. Ion source temperature: 200 °C.

3.1.4. NMR-spectroscopy

NMR measurements were carried out with a Bruker WM 500 instrument using TMS as internal standard.

3.1.5. Polarimetry

Measurements were carried out with a Polarimeter 341 (Perkin Elmer) at 589 nm at 20 °C. Due to very small amounts of isolated compounds only the sense of optical rotation is given to avoid inaccuracies.

Rearrangement reaction of (+)-**2** and (+)-**3** was performed at room temperature in benzene by addition of acidic ion exchange resin Amberlyst®15. A sample was taken after 30 min and analysed by GC and GC–MS.

Dehydration of (+)-**4** was performed at 0 °C in pyridine/chloroform (1:1) by addition of thionyl chloride during 40 min. The reactions was quenched by addition of saturated aq. $NaHCO_3$ solution. The aqueous layer was extracted three times with chloroform. The organic layer was washed twice with saturated aq. $NaHCO_3$ solution and dried over anhydrous $MgSO_4$ prior to GC and GC–MS investigation.

3.2. Plant material and essential oils

Solidago canadensis was collected at Szczyrk near Kattowice (Poland) in June 2001. The essential oils of the plant were obtained by hydrodistillation (2 h) of the fresh green parts of the plant using ca. 1 ml of n-hexane as collection solvent.

3.3. Isolation of single constituents of the essential oil

The isolation was carried out using preparative GC: The oil of *Solidago cadensis* was fractionated by prep. GC using an SE-30 column at 100 °C with a heating rate of 2 °C/min and yielded **2** and **3** in one fraction. The single compounds were obtained from that fraction using a column with heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin (110 °C isothermal). **4** was isolated from the essential oil using a column with SE 30 as stationary phase.

3.3.1. 6-epi-α-Cubebene (2)

3aα,3bβ,4,5,6,7-hexahydro-3,7-dimethyl-4-(1-methylethyl)-1H-cyclopenta[1,3]cyclopropa[1,2]benzene, colourless oil, RI_{CPSIL5}:1412, sense of optical rotation (benzene): (+); ^1H NMR (500.1 MHz, C_6D_6): $\delta = 0.55$–0.59 (*m*, 1H, H-6), 0.64–0.72 (*m*, 1H, H-8a), 0.93 (*d*, 3H, H-12, $J = 6.1$ Hz), 0.89–1.04 (*m*, 1H, H-9a), 1.02 (*d*, 3H, H-13, $J = 5.9$ Hz), 1.07 (*d*, 3H, H-14, $J = 7.1$ Hz), 1.26–1.30 (*m*, 1H, H-5), 1.37–1.46 (*m*, 3H, H-7, H-8b, H-11), 1.46–1.53 (*m*, 1H, H-9b), 1.79 (*dd*, 3H, H-15, $J = 2.0$, 4.0

Hz), 1.82–1.92 (*m*, 1H, H-10), 2.26–2.35 (*m*, 1H, H-2a), 2.62–2.70 (*m*, 1H, H-2b), 4.98 (*d*, 1H, H-3, $J=1.5$ Hz); ^{13}C NMR (125.75 MHz, C_6D_6): $\delta=16.86$ (*q*, C-15), 20.19 (*q*, C-14), 21.08 (*q*, C-13), 21.12 (*q*, C-12), 23.99 (*t*, C-8), 31.88 (*d*, C-10), 32.73 (*s*, C-1), 32.98 (*t*, C-9), 33.85 (*d*, C-11), 35.28 (*d*, C-6), 35.86 (*d*, C-5), 40.53 (*t*, C-2), 41.16 (*d*, C-7), 120.73 (*d*, C-3), 145.20 (*s*, C-4); MS (EI, 70 eV), *m*/*z* (rel. Int.): 39 (16), 41 (46), 43 (16), 55 (24), 77 (20), 79 (28), 81 (20), 91 (45), 93 (23), 105 (46), 107 (22), 119 (23), 120 (100), 121 (16), 161 (72), 204 (12).

3.3.2. 6-epi-β-Cubebene (**3**)

2,3,3aα,3bβ,4,5,6,7-Octahydro-7-methyl-3-methylene-4-(1-methylethyl)-1H-cyclopenta[1,3]cyclopropa[1,2]benzene, colourless oil, RI_{CPSIL5}:1449, sense of optical rotation (benzene): (+) ; ^{1}H NMR (500.1 MHz, C_6D_6): $\delta=0.63$–0.72 (*m*, 1H, H-8a), 0.80–0.90 (*m*, 1H, H-9a), 0.91 (*d*, 3H, H-13, $J=6.3$ Hz), 1.01 (*d*, 6H, H-12, H-14, $J=6.0$ Hz), 1.08–1.12 (*m*, 1H, H-6), 1.36–1.44 (*m*, 3H, H-7, H-8b, H-11), 1.44–1.49 (*m*, 2H, H-5, H-9b), 1.63 (*dd*, 1H, H-2a, $J=8.2$, 12.0 Hz), 1.73–1.82 (*m*, 2H, H-2b/H-10), 1.86–1.96 (*m*, 1H, H-3a), 2.05 (*dd*, 1H, H-3b, $J=9.1$, 16.7 Hz), 4.80 (*s*, 1H, H-15a), 4.99 (*s*, 1H, H-15b); ^{13}C NMR (125.8 MHz, C_6D_6): $\delta=19.94$ (*q*, C-14), 20.86 (*q*, C-12), 20.89 (*q*, C-13), 23.52 (*t*, C-8), 27.49 (*d*, C-6), 29.16 (*t*, C-3), 31.17 (*t*, C-2), 31.34 (*d*, C-10), 32.94 (*t*, C-9), 33.44 (*d*, C-11), 33.93 (*d*, C-5), 36.00 (*s*, C-1), 40.72 (*d*, C-7), 101.46 (*t*, C-15), 154.47 (*s*, C-4); MS (EI, 70 eV), *m*/*z* (rel. int.): 39 (18), 41 (50), 43 (16), 55 (29), 77 (20), 79 (27), 81 (25), 91 (48), 93 (23), 105 (51), 107 (20), 119 (27), 120 (100), 121 (15), 161 (90), 204 (12).

3.3.3. 6-epi-Cubenol (**4**)

1-Isopropyl-4,7-dimethyl-1,3,4,5,6,8a-hexahydro-2*H*-naphthalene-4a-ol, colourless oil, RI_{CPSIL5}: 1602, sense of optical rotation (benzene): (+); ^{1}H NMR (400.1 MHz, C_6D_6): $\delta=0.84$ (*d*, 3H, CH_3-10, $J=6.6$ Hz), 0.92 (*d*, 3H, CH_3-11, $J=6.1$ Hz), 0.95 (*d*, 3H, CH_3-11, $J=6.1$ Hz), 0.89–0.96 (*m*, 1H, H-8a), 1.33–1.56 (*m*, 5H, H-2a, H-7, H-9a,b, H-11), 1.56–1.61 (*m*, 4H, CH_3-4, H-10), 1.62–1.69 (*m*, 1H, H-8b), 1.75–1.83 (*m*, 3H, H-2b, H-3a,b), 2.45 (*br. s*, 1H, H-6), 5.28 (*br. s*, 1H, H-5); ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta=0.86$ (*d*, 3H, CH_3-10, $J=6.9$ Hz), 0.90 (*d*, 3H, CH_3-11, $J=6.6$ Hz), 0.94 (*d*, 3H, CH_3-11, $J=6.4$ Hz), 0.90–0.97 (*m*, 1H, H-8a), 1.19–1.36 (*m*, 3H, H-3a, H-7, H-9a), 1.38–1.46 (*m*, 1H, H-8b), 1.48–1.58 (*m*, 2H, H-2a, H-11), 1.61–1.69 (*m*, 4H, CH_3-4, H-8b, H-10), 1.88–2.05 (*m*, 2H, H-2b, H-3b), 2.42 (*br. s*, 1H, H-6), 5.20 (*br. s*, 1H, H-5); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta=14.8$ (*q*, C-14), 20.7 (*q*, C-12), 21.9 (*q*, C-13), 23.4 (*q*, C-15), 26.8 (*t*, C-8), 28.9 (*d*, C-11), 29.9 (*t*, C-3), 30.9 (*d*, C-10), 31.0 (*t*, C-9), 35.1 (*t*, C-2), 42.7 (*d*, C-7), 45.6 (*d*, C-6), 71.8 (*s*, C-1), 121.1 (*d*, C-5), 134.7 (*s*, C-4); MS (EI, 70 eV), *m*/*z* (rel. int.): 39 (36), 41 (100), 43 (83), 53 (25), 55 (41), 77 (28), 79 (27), 81 (29), 91 (35), 93 (26), 105 (33), 119 (25), 161 (45), 179 (77), 204 (12), 222 (2).

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