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Syntheses in the Isocamphane Series XLI [1]. Derivatives of Epoxyisocamphenilanic Acid, Epoxycamphene, and a New Access to 7-*syn*-Hydroxycamphene[a]

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Summary. The syntheses of the title compounds are described. Epoxidation of the endocyclic norbornene double bond leads to a series of epoxy derivatives of this class of terpenic compounds, which on account of their biological decomposability might turn out to be valuable microbiocides. Cleavage of the epoxide bridge of 5,6-epoxy-camphene opens a new access to the fragrance compound 7-*syn*-hydroxy-camphene *via* a rearrangement.

Keywords. 2-Acetyl-3,3-dimethyl-norbornene; Bicyclo[2.2.1]heptane derivatives; Epoxides; Fragrance compounds; Monoterpene derivatives.

Synthesen in der Isocamphanreihe, 41. Mitt. [1]**. Derivate der Epoxyisocamphenilansäure, Epoxycamphen und ein neuer Zugang zu 7-*syn*-Hydroxycamphen.**

Die Synthese der Titelverbindungen wird beschrieben. Epoxidierung der endocyclischen Doppelbindung in 2-Acetyl-3,3-dimethyl-norbornen führt zu einer Reihe von Epoxyderivaten dieser terpenoiden Verbindungen, die sich wegen ihrer biologischen Abbaubarkeit als wertvolle Mikrobiozide erweisen könnten. Öffnung des Epoxidringes in 5,6-Epoxycamphen ermöglicht über eine Umlagerung einen neuen Zugang zu 7-*syn*-Hydroxycamphen.

Introduction

In continuation of our studies to use the bicyclic ketone 2-acetyl-3,3-dimethylnorborn-5-ene (**1**) [2] as an easily accessible starting material for the preparation of either fragrants [3–5], pharmaca [6], or fungicides with the biologically decomposable terpenic skeleton [7, 8], we focused our interest on the endocyclic double bond of the norbornene nucleus whose cleavage leads to fragrance compounds [5] or desoxysugars with a cyclopentane ring [9]. Moreover, epoxidation of its double bond proves to be a very useful tool for further

[a] Dedicated to Prof. Dr. *G. Heinisch* on the occasion of his 60th birthday

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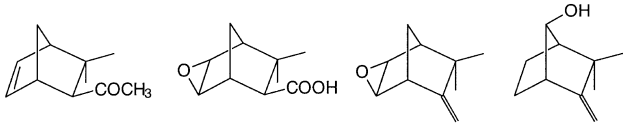
functional group inversions, thus establishing other pharmacophoric groups. Regarding the epoxide function, it has to be noticed that it shows remarkable cytostatic and excellent microbiocidal activities [10, 11]. Therefore, a combination of this cell alkylating group with the fungicidal properties of isocamphenilanic acid derivatives [8] should furnish more potent but still easily decomposable fungicides. This holds also for the naturally occurring monoterpenic hydrocarbon camphene whose bacteriostatic and fungicidal properties are known as well [12, 13].

In this paper we report the preparation of derivatives of the title compound 5,6-epoxy isocamphenilanic acid (**2**) as well as the synthesis of 5,6-epoxy camphene (**3**), and finally the dissection of the remarkably stable epoxide ring of **3** which opens a new access to the mild camphoraceous smelling 7-*syn*-hydroxy camphene (**4**) *via* a rearrangement.

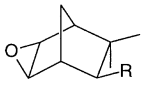


1 **2** **3** **4**

Results and Discussion

Derivatives of 5,6-epoxy-isocamphenilanic acid

5,6-Epoxy-isocamphenilanic acid (**2**) was prepared according to our earlier procedure [14], but now in a better yield because we started from pure **1**. We are now also able to supplement the structural determination of **2** with a detailed NMR spectroscopic characterization of this norbornene oxide derivative. The *exo* position of the ether bridge in position 5,6 of the norbornane nucleus is ascertained by its ^{1}H NMR spectrum: no coupling of the ether protons C5-H and C6-H with C4-H or C1-H could be detected, thus proving the *exo* position of the epoxide; with the epoxide protons in equatorial ($=$*exo*) position and hence the ether bridge in *endo* position, a coupling constant of about 4 Hz would have been expected [15]. The vicinal coupling of both *endo*-H at C5 and C6 (about 9 Hz) also corresponds with known data, whereas a similar ^3J of the *exo*-H at C5 and C6 should have amounted to about 12 Hz [15]. Esterification of **2** with diazomethane furnished the epoxy ester **5** which could be reduced to the primary alcohol **6** using $LiAlH_4$. The steric shielding effect of the methylene bridge on the epoxide ring leads to a



5: *R* = $COOCH_3$
6: *R* = CH_2OH
7: *R* = CHO
8: *R* = CH=N-NH-Tos
9: *R* = CH_2OCOCH_3
10: *R* = CH_2OTos
11: *R* = $CON(C_2H_5)_2$
12: *R* = $CH_2N(C_2H_5)_2$
13: *R* = $CH_2N(C_2H_5)_2$ with O

remarkable stability against this strong reducing reagent [16]. By oxidation of **6** with pyridinium chlorochromate, 5,6-epoxy-isocamphenilanal (**7**) was obtained which could be transformed into its tosylhydrazone **8** without difficulties. Esterification of 5,6-epoxy-isocamphenilanol (**6**) with acetic anhydride/pyridine yielded the corresponding acetate **9**, whereas with tosyl chloride/*DMAP*/pyridine the tosylate **10** was obtained.

5,6-Epoxy-camphene

The easy access of **2** prompted us to synthesize the monoterpene derivative 5,6-epoxy-camphene (**3**). We have found a way to transform the carboxyl group at C2 of the bicyclus into the exocyclic double bond of camphene without any arrangement of the sensible monoterpene [17]. On account of the sensitivity of the epoxide function against $SOCl_2$, the conventional way to prepare an acid amide was not possible. Therefore, another method for a direct conversion of **2** into its diethyl amide **11** had to be found. By using hexachloro-cyclo-triphosphatriazene [18] in ethyl acetate/triethyl amine the carboxyl function of **2** could be activated to react directly with diethyl amine to the tertiary diethyl amide **11** which in turn could be reduced to the corresponding amine **12** by $LiAlH_4$ without difficulties. Afterwards, **12** was transformed into its N-oxide **13** by methanolic H_2O_2 at 0°C. Finally, pyrolysis of **13** furnished the target molecule **3**, which exerted a warm and pleasant camphoraceous odour. The results of the biological screening of the epoxides with respect to their fungicidal and bacteriostatic properties will be reported elsewhere.

7-syn-Hydroxycamphene

As already mentioned, the epoxide function enables the hydroxylation of double bonds by reductive opening of the cyclic ether bridge. Surprisingly, this epoxide resisted several efforts to cleave it: either **3** could be regained without damage, or a nearly inseparable multi-component mixture was the result. A similar outcome has been reported by *Gassman et al.* for the opening of 2,3-epoxy-1,7,7-trimethyl-bicyclo[2.2.1]heptane by trimethyl silyl cyanide/ZnI_2 [19]. With Zn/trimethylsilyl chloride/dichloromethane or Li/ethylenediamine [20], a three-component reaction mixture was obtained, although such a reduction of norbornene oxides without rearrangement has been reported [21]. By HPLC it was possible to isolate one single compound pure enough to elucidate its structure by spectroscopic methods.

Though **4** has been prepared for the first time unambiguously already in 1958 by *van Tamelen et al.* [22], no NMR spectroscopic data of this camphene alcohol could be found; only 7-*anti*-hydroxycamphene has been described roughly in Ref. [23]. The signals of the protons of the exocyclic double bond could be detected in the ^1H NMR spectrum of **4** at 4.56 and 4.75 ppm and that of the carbinol proton at 4.46 ppm. These data are in agreement with the structure of a hydroxy camphene as well as most of the chemical shifts in the ^{13}C NMR spectrum. The carbinol signal could be found at 78.1 ppm. Two highfield signals of CH_2 groups at 20.5 and 25.7 ppm clearly point at the C-atoms C5 and C6. On account of the good

congruence of the shifts of C1, C2, C3, C4, and both methyl carbon atoms of this camphene derivative with those of the corresponding C-atoms in 5-hydroxy-1-methyl-camphene [24] or the parent compound itself, the hydroxyl group can be assigned only to the bridge-C7. Irradiation of the proton 1-H at 2.6 ppm in the ^{1}H NMR spectrum resulted in a decrease of the signal width of the carbinol proton indicating the position of the hydroxyl group at C7. Finally, the absence of a W-coupling [15, 25] with the *endo*-proton at C6 as well as an NOE of the carbinol proton towards the olefinic protons of the exocyclic double bond are compatible with the *syn*-position of the hydroxyl group at C7 and the *anti*-position of its carbinol proton. Such rearrangements with an anchimeric assistance by π-electrons of the double bond *via* a non-classical ion are encountered very often either in the terpene field [23, 26, 27] or with norbornene oxides [28, 29].

7-*syn*-hydroxycamphene (**4**) is characterized by a warm, soft and very pleasant camphoraceous odour which harmonizes well with woody and ''fougere'' notes.

Experimental

IR spectra: Perkin-Elmer 237; GC: VAE-3700 and Shimadzu 14A, column: SE 30 DF 0.25; NMR spectra: Bruker AC 80 and Bruker WM 250, *TMS*; MS: Varian MAT CH 7 (70 eV); melting points (uncorrected): Kofler Heiztischmikroskop; HPLC: Beckmann 112, detector GAT-LCD 201 (differential refractometer), column KG S5W; TLC: aluminum foil, silica gel 60 F_{254}, 20×20 cm, 0.2 mm layer thickness, Merck, no. 5717; preparative TLC: silica gel 60 F_{254}S with concentration zone, 20×20 cm, 2 mm layer thickness, Merck, no. 13793.

3,3-Dimethyl-5,6-epoxy-bicyclo[2.2.1]hept-2-exo-yl carboxylic acid methyl ester (**5**; $C_{11}H_{16}O_3$)

To a solution of 12.45 g (68.5 mmol) **2** [14] in $CH_3OH/H_2O = 10:1$, diazomethane was added in the usual manner, and the reaction mixture stirred for 1 h at room temperature. Workup yielded 11.86 g (88.5%) of **5** as a colourless liquid with camphoraceous odour.

B.p.$_{0.5}$: 97°C; $n_D^{25} = 1.4840$; IR (KBr): 1750, 1200, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 80 MHz): 0.90, 1.21 (2s, gem. CH_3), 2.63 (C1-H, m), 3.11, 3.32 (C5-H, C6-H, 2m), 3.59 (ester methyl, s, 3H) ppm; MS: *m/z* (r.I.) = 196 (M^+, 1), 181(2), 165(9), 151(1), 136(10), 115(100), 107(16), 105(6), 95(8), 93(12), 91(14), 82(86), 79(13), 67(8).

3,3-Dimethyl-5,6-epoxy-bicyclo[2.2.1]hept-2-exo-yl methanol (**6**; $C_{10}H_{16}O_2$)

To a suspension of $LiAlH_4$ (40.5 ml, 40.46 mmol) in 30 ml of dry diethyl ether, a solution of **5** (11.8 g, 71 mmol) in 100 ml dry diethyl ether was added slowly keeping the solvent moderately boiling. After refluxing for 4 h and slow addition of ice water the mixture was worked up as usual.

Yield: 9.6 g (95%); white crystals; m.p.: 128°C; IR (KBr): 3400, 1250, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 80 MHz): 1.00, 1.15 (2s, gem. CH_3), 3.25, 3.40 (C5-H, C6-H, 2m), 3.63 (CH_2OH, m, 2H) ppm; MS: *m/z* (r.I.) = 168 (M^+, 0.1), 135(1), 109(3), 107(8), 105(5), 95(5), 93(7), 91(11), 81(100), 79(15), 67(14), 41(17).

3,3-Dimethyl-5,6-epoxy-bicyclo[2.2.1]hept-2-exo-yl carbaldehyde (**7**; $C_{10}H_{14}O_2$)

A mixture of 20.4 g (93.84 mmol) pyridinium chlorochromate [30], 1.49 g (18.16 mmol) dry sodium acetate in 82 ml of dry CH_2Cl_2, and 10.2 g (61.2 mmol) **6** in 82 ml of the same solvent was stirred for

3 h. After addition of 1500 ml of dry diethyl ether the suspension was filtered through silica gel and set free from the solvent by evaporation. The residue was distilled in a *Kugelrohr*.

B.p.$_{0.5}$: 78°C; yield: 9.33 g (92.6%); white crystals; m.p.: 138°C; IR (KBr): 2700, 1710, 1250, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 80 MHz): 1.05, 1.15 (2s, gem. CH_3), 2.41 (C2-H, d, $J = 7$ Hz), 3.22, 3.39 (C5-H, C6-H, 2m), 9.8 (CHO, d, $J = 7$ Hz) ppm; MS: *m/z* (r.I.) = 166 (M^+, 0.4), 151(1), 137(2), 123(2), 119(2), 107(5), 95(8), 93(7), 91(12), 81(100), 79(13), 77(14), 67(24), 41(55).

3,3,-Dimethyl-5,6,epoxy-bicyclo[2.2.1]hept-2-exo-yl carbaldehyde tosyl hydrazone (**8**; $C_{17}H_{22}N_2O_3S$)

A solution of 9.33 g (56 mmol) of **7** in 60% CH_3OH was added slowly to a mixture of 10.35 g (56 mmol) tosylhydrazide in 20 ml of the same solvent at 60°C and stirred till cooling. This mixture was put in a refrigerator overnight. Afterwards, the semicrystalline product was purified by column chromatography over silica gel (CH_2Cl_2: ethyl acetate = 10:2).

Yield: 10.2 g (54.3%); white crystals; m.p.: 53–55°C; IR (KBr): 3450, 1610, 1325, 1250, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 80 MHz): 0.65, 1.05 (2s, gem. CH_3), 2.40 (s, aromatic CH_3), 7.01 (= CH, d, 1H, $J = 7$ Hz), 7.2, 7.7 (aromatic H, 4H), 7.9 (NH, s) ppm; MS: *m/z* (r.I.) = 186 ($M^+ - 150$, 1), 172(2), 157(6), 150 ($M^+ - 186$, 1), 139(21), 107(15), 105(6), 95(6), 91(100), 81(36), 79(29), 71(72), 51(21), 39(64).

3,3-Dimethyl-5,6-epoxy-bicyclo[2.2.1]hept-2-exo-yl-methylacetate (**9**; $C_{11}H_{18}O_3$)

A mixture of 3.32 g (32.5 mmol) freshly distilled acetic anhydride, 3.09 g (39 mmol) dry pyridine, and 5.47 g (32.5 mmol) **6** was refluxed for 3 h and poured into ice water afterwards. Usual workup yielded 5.07 g (78.5%) of a colourless, oily liquid.

$n_D^{25} = 1.4828$; IR (NaCl, liquid film): 1750, 1380, 1250, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 80 MHz): 1.00, 1.11 (2s, gem. CH_3), 2.01 (s, 3H, -$OCOCH_3$), 3.28, 3.38 (C5-H, C6-H, 2m), 4.02 (m, 2H, -CH_2-OCO-) ppm; MS: *m/z* (r.I.) = 210 (M^+, 2), 193(5), 150(13), 135(12), 121(23), 107(26), 82(85), 81(100), 43(93).

3,3-Dimethyl-5,6-epoxy-bicyclo[2.2.1]hept-2-exo-yl-methyl-tosylate (**10**; $C_{17}H_{22}O_4S$)

1.00 g (5.9 mmol) **6** in 9 ml dry pyridine was added to a cooled (0°C) mixture of 2.43 g (12.35 mmol) tosyl chloride and 4.5 ml 4-dimethylamino-pyridine in 10 ml of the same solvent and stirred for 15 h at room temperature. After addition of ice water the mixture was extracted with CH_2Cl_2 and worked up as usual.

Yield: 1.26 g (66%); white crystals; m.p.: 91°C; ^{1}H NMR ($CDCl_3$, δ, 80 MHz): 0.85, 1.12 (2s, gem. CH_3); 1.78 (m, C2-H), 2.54 (s, arom. CH_3), 3.28, 3.40 (C5-H, C6-H, 2m), 4.77 (-CH_2O-, d, $J = 8$ Hz), 7.35, 7.81 (2m, 4H), ppm; MS: *m/z* (r.I.) = 322 (M^+, 4), 292(4), 264(3), 173(2), 172(1), 167(4), 155(19), 151(21), 150(73), 135(13), 121(35), 94(100).

3,3-Dimethyl-5,6-epoxy-bicyclo[2.2.1]hept-2-exo-yl carboxylic acid-N,N-diethyl amide (**11**)

3.25 g (0.93 mmol) hexachlorocyclotriphosphatriazene (Aldrich) in 50 ml ethyl acetate were added to a solution of 1.7 g (9.34 mmol) **2** and 943 mg (9.34 mmol) triethylamine in 70 ml of ethyl acetate under vigorous stirring which was continued for another 10 min. Then, 6.82 g (9.3 mmol) diethylamine was added and again stirred for about 10 min. Afterwards, a saturated $NaHCO_3$ solution was added to the mixture followed by extraction with diethyl ether. The organic layers were washed with H_2O, diluted HCl, again with H_2O, dried over Na_2SO_4, and freed from the solvent by evaporation. The residue was purified by crystallization with *n*-pentane.

Yield: 1.1 g (50%); white crystals; m.p.: 118–120°C; IR (KBr): 1630, 1230, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, δ, 80 MHz): 0.90, 1.11 (2s, gem. CH_3), 1.21, 1.35 (CH_3 of the amide, 2t), 2.61 (C1-H, m), 3.20–3.40 (C5-H, C6-H, N-CH_2-CH_3, broad m, 4H) ppm; MS: *m/z* (r.I.) = 237 (M+, 21), 222(1), 165(6), 156(100), 137(8), 107(13), 100(97), 83(74), 73(11), 58(37), 41(26).

3,3-Dimethyl-5,6-epoxy-bicyclo[2.2.1]hept-2-exo-yl-diethylaminomethane (**12**)

To a suspension of 7.4 ml $LiAlH_4$ (= 0.27 g $LiAlH_4$, 7.1 mmol), a solution of 2 g (8.4 mmol) amide (**11**) dissolved in dry diethyl ether was added under an atmosphere of dry Ar at 0°C and with vigorous stirring. After refluxing for a period of 5 h the mixture was worked up as usual. Upon *Kugelrohr* distillation, 0.82 g (43.6%) of **12** were obtained.

Colourless liquid; b.p.$_{0.1}$: 150°C; $n_D^{20} = 1.4889$; IR (NaCl, liquid film): 1380, 1360, 1200, 900 cm^{-1}; ^1H NMR ($CDCl_3$, δ, 80 MHz): 0.91, 1.12 (2s, gem. CH_3), 1.2, 1.3 (2t, N-CH_2-C*H*$_3$), 2.30 (m, 2H, -CH_2-N-), 2.45 (2q, 4H, N-C*H*$_2$-CH_3), 2.61 (m, C1-H), 3.21, 3.40 (C5-H, C6-H, 2m) ppm; MS: *m/z* (r.I.) = 223 (M^+, 2), 207(2), 86(100), 73(2), 58(10), 41(5).

3,3-Dimethyl-5,6-epoxy-2-methylene-bicyclo[2.2.1]heptane, (5,6-epoxycamphene) (**3**; $C_{10}H_{14}O$)

a) 1 g (4.4 mmol) amine **12** was dissolved in 1.6 ml CH_3OH and cooled to −5°C. To this solution, 1.6 ml 30% H_2O_2 (14.7 mmol) dissolved in 1.6 ml 50% CH_3OH were added, and the mixture was stirred for 5 h. Afterwards, 80 mg 10% Pd on charcoal were added, and stirring was continued for about 1 h. Further workup according to Ref. [17] yielded 1.1 g (100%) of crude **13** as semi-solid, glassy crystals.

b) 1.1 g (4.2 mmol) **13** were mixed very thoroughly with fine glas pearls (diameter: 0.2 mm) and pyrolyzed at 100°C in a *Kugelrohr* apparatus. By fractionated distillation of this pyrolysate, 650 mg (94.5%) of **3** were obtained as a colourless liquid.

B.p.$_{0.1}$: 100°C; $n_D^{20} = 1.4842$; IR (NaCl, liquid film): 3040, 1660, 1380, 1360, 1250, 890 cm^{-1}; ^1H NMR ($CDCl_3$, δ, 80 MHz): 1.00, 1.20 (2s, gem. CH_3), 2.38 (m, C4-H), 2.63 (m, C1-H), 3.21, 3.41 (C5-H, C6-H, 2m), 4.7, 4.9 (2s, exocycl. $=CH_2$) ppm; MS: *m/z* (r.I.) = 150 (M^+, 0.5), 135(8), 121(10), 109(1), 107(10), 94(7), 93(9), 81(2), 67(100), 54(3), 41(23).

3,3-Dimethyl-2-methylene-bicyclo[2.2.1]heptane-7-syn-ol, 7-syn-hydroxycamphene (**4**; $C_{10}H_{16}O$)

Under Ar and with vigorous stirring, 60 mg (8.6 mmol) of finely cut Li wire were dissolved in 3 ml of dry ethylene diamine and slowly mixed with 400 mg (2.6 mmol) of **3**. A strong exothermic reaction was noticed, therefore ice-water cooling was necessary. The end of the reduction was indicated by a change from deep blue to a bright violet colour. After addition of ice water and extraction with diethyl ether, the combined organic extracts were dried over Na_2SO_4 and finally freed from the solvent by evaporation. Yield of crude **4**: 350 mg (86%) as an oily liquid. Purification by preparative TLC (silica gel $KG60F_{254}$, pentane:ethyl acetate = 80:20) and by HPLC (1 ml/min, 30 bar, toluene:ethyl acetate = 80:20). From the three fractions, the second one crystallized upon evaporation of the solvent.

Yield: 53 mg (13%); white crystals; m.p.: 88–89°C; IR (NaCl, liquid film): 3400, 3030, 1380, 1360 cm^{-1}; ^1H NMR ($CDCl_3$, δ, 80 MHz): 0.90, 1.09 (2s, gem. CH_3), 2.63 (m, C1-H), 4.46 (d, -C*H*-OH), 4.56, 4.75 (2s, exocycl. $=CH_2$) ppm; ^{13}C NMR ($CDCl_3$, δ, 250 MHz): 163.08, 101.5 (C2, C8), 78.10 (C7), 51.49, 52.31, 51.49 (C1, C4), 29.40 (C3), 26.10 (CH_3), 25.70 (C6), 20.52 (C5), 18.81 (CH_3) ppm; MS: *m/z* (r.I.) = 152 (M^+, 12), 137(32), 123(20), 91(46), 82(25), 81(100), 68(18), 55(55), 41(92).

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