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80. Synthesis of 3,7-Diacetoxy-benzo-bullvalene[1])

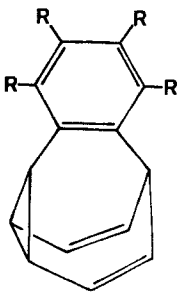
by **Christopher B. Chapleo**[2]) and **André S. Dreiding**
Organisch-Chemisches Institut der Universität Zürich, Rämistrasse 76, 8001 Zürich

(29. XII. 75)

Zusammenfassung. Durch partielle reduktive Fragmentierung von 9,9a-Benzo-9a-homotriaster-9-en-3,7-dion (**6**) mit Zinkstaub in Eisessig wurde 61% 9,10-Benzo-tricyclo[3.3.2.$0^{2,8}$]-dec-9-en-3,7-dion (**3**) und daraus mit Isopropenyl-acetat 47% 3,7-Diacetoxy-benzo-bullvalen (**4**) erhalten. Eine relativ schnelle degenerierte *Cope*-Umlagerung in **4** liess sich durch die Temperaturabhängigkeit von dessen ^{1}H-NMR.-Spektrum aufzeigen. Mildere Acetylierung von **3** lieferte das Mono-enolacetat **9**.

Unter etwas energischeren Bedingungen der Zink/Eisessig-Reduktion wurden beide Cyclopropanringe in **6** aufgespalten, wobei 90% eines Gemisches, hauptsächlich bestehend aus 9,10-benzo-bicyclo[3.3.2]dec-9-en-3,7-diol (**7**) entstand. Behandlung von **6** mit Zinkstaub in Acetanhydrid lieferte – offenbar wegen noch unübersichtlichen Unterschieden in den Reaktionsbedingungen – einmal 50% des oben erwähnten tricyclischen Diketons **3**, ein andermal 45% 3,8-Diacetoxy-9,10-benzo-bicyclo[3.3.2]deca-2,9-dien-7-on (**10**) und sonst Gemische von **3** und **10**, sowie von einem Produkt, für das die Struktur eines 3,7-Diacetoxy-9,10-benzo-tricyclo[3.3.2.$0^{2,8}$]dec-9-en – Diastereomerengemisches **11** in Betracht gezogen wird.

Benzo-bullvalene **1** has been prepared from benzobarbaralone over a ring expansion [1] and from 7,8-benzo-bicyclo[4.2.2]deca-2,4,7,9-tetraene by a photochemical method [2]. It was shown, from the ^{1}H-NMR. spectrum, that the benzene ring of benzo-bullvalene **1** does not participate in the degenerate *Cope* rearrangement, as



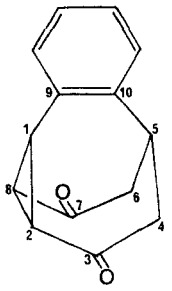
1 R = H
2 R = C_6H_5

[1]) The systematic name is: 3,7-diacetoxy-9,10-benzo-tricyclo[3.3.2.$0^{2,8}$]deca-3,6,9-triene, which is used in the Experimental Part.

[2]) Post-doctoral fellow, University of Zürich, 1972–1975.

had already been found by *Oth et al.* [3] with (tetraphenyl-benzo)-bullvalene (**2**) and (hydroxy-benzo)-bullvalene.

The present paper describes our experience in the preparation of 9,10-benzo-tricyclo[3.3.2.$0^{2,8}$]dec-9-ene-3,7-dione (**3**) and its bis-enolacetate: 3,7-diacetoxy-benzo-bullvalene (**4**). The diketone **3** may be a precursor for other, in the thermal average symmetrically substituted, benzo-bullvalenes **5**.



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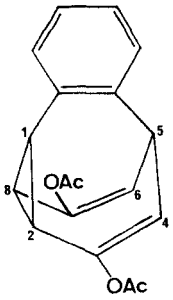

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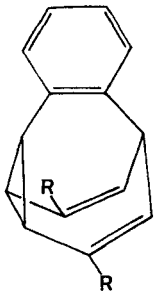

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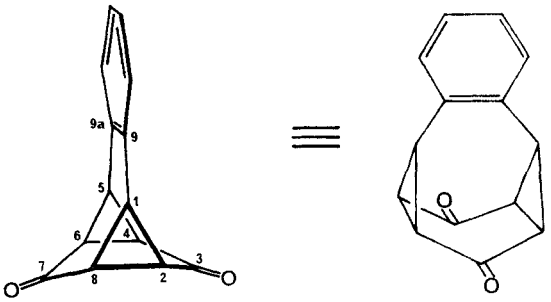
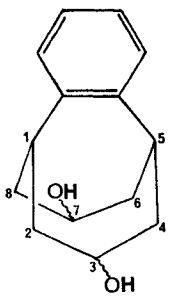
Recent work on the synthesis of benzo-homotriasterenedione **6** [4] provided us with a convenient starting material for the synthetic approach to **3**.



6

In earlier work from our laboratories [5] it was noted that zinc reduction of a brominated triasteranedione led to a bicyclic compound as a result of both of the cyclopropane rings being opened by a reaction analogous to the known [6] fragmentation of γ-diketones. It was envisaged that this process might be controlled so as to open only one cyclopropane ring of **6**.

This was accomplished by treatment of 9,9a-benzo-9a-homotriaster-9-ene-3,7-dione (**6**) with zinc in acetic acid for 5 h to yield the required 9,10-benzo-tricyclo-[3.3.2.$0^{2,8}$]dec-9-ene-3,7-dione (**3**), m.p. 138°, along with 10% of a by-product which is presumed to be 9,10-benzo-bicyclo[3.2.2]dec-9-ene-3,7-diol (**7**). A longer reaction time afforded only 5% of the diketone **3** while the major product was the diol **7**, the configurational purity of which was not established. The diol was oxidized to give 45% of the known 9,10-benzo-bicyclo[3.2.2]dec-9-ene-3,7-dione, isolated in form of the diketone **8** after sublimation (*cf.* [4] [7]).



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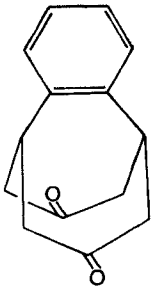

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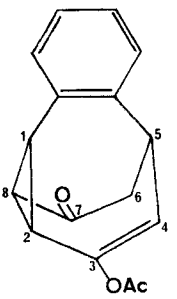
The structure of the tricyclic dione **3** was deduced from its properties: Elemental analysis and the mass spectrum (M^+ 212 *m/e*) correspond to the molecular formula $C_{14}H_{12}O_2$. The IR. spectrum shows a carbonyl absorption at 1685 cm^{-1}, which is also characteristic of the triasteranones. The ^{1}H-NMR. spectrum contains only three absorptions in the ratio 4:1:7. The multiplet at $\delta = 7.5$–7.0 belongs to the four aromatic hydrogen atoms and the one-proton double doublet ($J = 4$ and 8) at $\delta =$ 3.18 is assigned to the benzylic H–C(5). The signals for the other seven hydrogen atoms fall together under the multiplet at $\delta = 3.1$–2.7.

This key intermediate **3** was readily converted to the title compound **4**, m.p. 169°, in 47% yield using isopropenyl acetate with an acid catalyst. That the product was 3,7-diacetoxy-benzo-bullvalene (**4**) was evident from the spectral data, namely the M^+ peak at 296 *m/e* ($C_{18}H_{16}O_4$) as well as fragmentations with consecutive loss of two ketene molecules in the mass spectrum, the single IR. band at 1758 cm^{-1} and the temperature dependant ^{1}H-NMR. spectrum which demonstrates the fast and reversible valence isomerization of **4**.

At room temperature the ^{1}H-NMR. spectrum shows four signal groups in the ratio 2:1:2:3, the two middle signals being rather broad. Only at 60° does a thermal average of the valence isomers become apparent by a broad signal in the range of $\delta = 6$–2 resulting from the site exchange of the two cyclopropyl (H–C(2), H–C(8)) with the two olefinic hydrogen atoms (H–C(4), H–C(6)) and by a broadened triplet ($J = 8$) at $\delta = 3.18$ resulting from the site exchange of the two benzylic hydrogen atoms, namely H–C(1) with H–C(5). Below −10° the degenerate rearrangement is shown to be 'frozen', as now six signal groups and their couplings are clearly visible: As in the two spectra at higher temperatures the aromatic hydrogen atoms appear – here slightly broadened – as a multiplet at $\delta = 6.8$–7.6 and the two acetate methyl groups as a singlet at $\delta = 2.14$. New in this spectrum are the doublet ($J = 10$) at $\delta = 5.70$ for the two olefinic hydrogen atoms (H–C(4), H–C(6)), the one-proton triplet ($J = 10$) at $\delta = 3.52$ for the allylic-benzylic hydrogen atom (H–C(5)), the two-proton doublet at $\delta = 2.50$ and the one-proton triplet at $\delta = 3.00$ for the two equivalent allylic (H–C(2), H–C(8)) and the one benzylic (H–C(1)) cyclopropane hydrogen atoms respectively, both of the latter signals showing the coupling of 8 Hz, characteristic for *cis*-located hydrogen atoms on a cyclopropane ring.

In one experiment the acetylation of **3** had not gone to completion, so that 3-acetoxy-9,10-benzo-tricyclo[3.3.2.$0^{2,8}$]deca-3,9-diene-7-one (**9**), m.p. 184°, was iso-

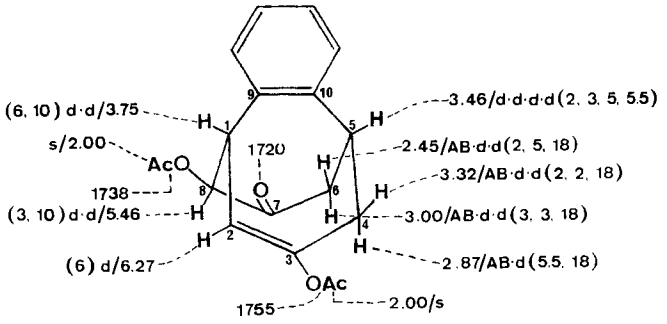
lated (in addition to recovered educt **3**). That the acetylation had only gone 'halfway' in this product could be seen in the mass spectrum with its M^+ at *m/e* 254, in the IR. spectrum with its two carbonyl absorptions at 1760 and 1680 cm^{-1} for acetoxy and ketone, and in the ^{1}H-NMR. spectrum with its one-proton double doublet (J = 3 and 10) at δ = 5.77 for H–C(4) and its three-proton singlet at δ = 2.06 for the acetoxy methyl group.



9

It was considered that the zinc reduction step leading to the diketone **3** and the bis-enol-acetate formation to give **4** might be achieved in one reaction. Hence the zinc reduction of **6** was performed in acetic anhydride so as to trap the enolate intermediate. In fact, the reaction depended (in a non-transparent way) on the acetic anhydride used. In one experiment it gave only the diketone **3** and no trace of **4**; in other experiments, using acetic anhydride purified in different ways, two other products were also isolated:

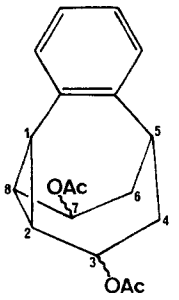
The first product was 3,8β-diacetoxy-9,10-benzo-bicyclo[3.3.2]deca-2,9-diene-7-one (**10**), m.p. 195°, isolated alone (45%) in one case. Elemental analysis and mass spectrum (M^+ 314 *m/e*) indicate the composition $C_{18}H_{18}O_5$ whilst the IR. spectrum shows the three different types of carbonyl absorptions required by structure **10**. Spin decoupling experiments assisted the ^{1}H-NMR. spectrum interpretation so that the assignments shown in the formula **10** were derived.



10

Molecular models show that the observed couplings are in agreement with those expected from the dihedral angles. Such long range couplings (due to W-arrangement)

as seen in the Hα–C(6)/Hα–C(8) and Hβ–C(6)/Hβ–C(4)[3]) signal pairs have been observed before in similar systems [8]. The diacetoxy-enone **10** is assumed to be formed by an attack of acetate ion on the cyclopropane carbon (f.i. C(8)) of **3**, producing a fragmentation of the C(8)–C(2) bond with formation of the C(2)–C(3)–O enolate system, which is then O-acetylated. This mechanism demands the β-configuration of the acetoxy group at C(8), as agrees with the signal ($\delta = 5.46$) of H–C(8), to which the α-configuration was assigned because of the large coupling ($J = 10$) with H–C(1) and the *W*-coupling ($J = 3$) with Hα–C(6).



11

The second product isolated in the zinc/acetic anhydride reduction has the following properties: Elemental analysis and mass spectrum (M^+ 300 *m/e*) show a molecular formula of $C_{18}H_{20}O_4$. The IR. spectrum has a single carbonyl band at 1730 cm^{-1} and no hydroxyl absorption. The ^{1}H-NMR. spectrum exhibits, aside from the signals of the four aromatic hydrogen atoms and of the two acetoxy methyl groups, only a triploid two-proton multiplet at $\delta = 3.4$–3.1 and an eight-proton multiplet at $\delta = 3.0$–2.3. The acetoxy methyl signal consists of two closely spaced singlets in the ratio of 3:1. The possibility is considered that this product may be a mixture of two diastereomers of 3,7-diacetoxy-9,10-benzo-tricyclo[3.3.2.$0^{2,8}$]dec-9-ene (**11**), even though the evidence is by no means conclusive.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *Sandoz AG*, Basel.

Experimental Part

1. General. – The abbreviations and the spectral data notations used here have been described previously [9]. ^{1}H-NMR.-Integration units are designated H instead of pr.

The mass-, ^{1}H-NMR. and IR. spectra were measured in our laboratories for mass spectrometry (direction Prof. *M. Hesse*), for nuclear magnetic resonance (direction Prof. *W. von Philipsborn* with Mr. *K. Bachmann*) and for micro analysis (direction *H. Frohofer*), respectively. Elementary analyses were performed in the last mentioned laboratory.

2. Reductions of 9,9a-benzo-9a-homotriaster-9-ene-3,7-dione (6). – 2.1. *With zinc in acetic acid.* A mixture of 0.06 g (0.29 mmol) of **6** and an excess of zinc dust (0.3 g) in 3 ml of glacial acetic acid was stirred at RT. for 5 h. It was then diluted with water and extracted with chloroform. The extracts were washed with 5% aqueous sodium carbonate, dried and evaporated to

[3]) We call that side of the eight membered ring which lies *cis* to the bridge carrying the benzene ring, the β-side and that *trans* to the bridge the α-side.

leave 0.06 g of a white solid. Purification by preparative TLC. on silica gel with chloroform/acetone 9:1 and recrystallization from chloroform/hexane gave 0.037 g (61%) of *9,10-benzo-tricyclo[3.3.2.0^{2,8}]dec-9-ene-3,7-dione* (**3**) as white plates, m.p. 136–138°. – IR. (KBr): 3055*w*, 3035*w*, 2925*w*, 2890*w*, 1685*s* (C=O); 1498*m*, 1388*m*, 1215*m*, 855*m*, 753*m*. – MS. 212/45 (M^+); 185/15; 184/92 (M^+ – CO); 183/30, 170/25, 169/45, 167/18, 157/18, 153/20, 142/47, 141/100, 129/30, 128/60, 116/38, 115/64. – ^{1}H-NMR. (100 MHz, $CDCl_3$): δ = 7.5–7.0/*m*, 4 H (aromatic H's); 3.18/*d* × *d* (*J* = 4 and 8), 1 H (H–C(5)); 3.1–2.7/*m*, 7 H (H–C(1), H–C(2), H–C(8), 2 × H–C(4), 2 × H–C(6)).

$C_{14}H_{12}O_2$ (212.24) Calc. C 79.22 H 5.70% Found C 79.42 H 5.94%

The ^{1}H-NMR. spectrum of the crude product indicated the presence of about 10% of a second compound, presumably **7** (see below).

When the time of the reaction was extended to 20 h, a crude product was obtained in 90% yield, which contained only about 5% of the diketone **3** (according to the ^{1}H-NMR. spectrum). The major component was not purified, but the signals of the mixture which we attributed to it are: ^{1}H-NMR. (60 MHz, $CDCl_3$): δ = 7.14/*s*, 4 H (aromatic H's); 3.77/br. *s*, 2 H (2 × OH); 3.13/br. *t* (*J* = 5), 2 H (H–C(3), H–C(7)); 3.0–1.8/*m*, 10 H (H–C(1), H–C(5), 2 × H–C(2), 2 × H–C(4), 2 × H–C(6), 2 × H–C(8)). The broadness of the triplet at δ = 3.13 (H–C(3), H–C(7)) makes it impossible to say whether the diol is one isomer or a mixture of isomers. This spectrum suggests that the major product is *9,10-benzo-bicyclo[3.2.2]dec-9-ene-3,7-diol* (**7**).

Oxidation of the above crude product with *Jones* reagent [10] in the usual way, followed by sublimation, gave a 45% overall yield of *9,10-benzo-bicyclo[3.2.2]dec-9-ene-3,7-dione* (**8**) whose m.p. and ^{1}H-NMR. spectrum were identical with an authentic sample [4] of the bicyclic dione **8**.

A reduction of **6** in the same way for 14 h resulted in an about 1:1 mixture (from ^{1}H-NMR. spectrum) of the tricyclic dione **3** and the bicyclic diol **7**.

2.2. *With zinc in acetic anhydride.* An excess of freshly activated zinc dust (0.25 g) was added to a stirred solution of 0.068 g (0.32 mmol) of **6** in 5 ml of acetic anhydride and the mixture was stirred at RT. for 24 h. Another 0.1 g of zinc dust was then added and after a further 24 h stirring the mixture was filtered and the zinc was washed with anhydrous benzene. The filtrate was evaporated to leave a brown oil which was dissolved in chloroform and the resulting solution was washed with water, dried and evaporated to give a partially crystalline residue. Purification by preparative TLC. on silica gel with chloroform/acetone 9:1 furnished 0.012 g (18%) of recovered **6** and 0.07 g of a crystalline product. Recrystallization of the latter from chloroform/hexane gave 0.046 g (45%) of *3,8β-diacetoxy-9,10-benzo-bicyclo[3.3.2]deca-2,9-diene-7-one* (**10**) as white plates, m.p. 193–195°. – IR. ($CHCl_3$): 3020*w*, 2918*w*, 2850*w*, 1755*s*, 1738*s*, 1720*s*, 1370*s*, 1220*s*, 1190*s*, 1103*s*, 1080*w*, 1015*m*, 958*m*. – MS. 314/1.5 (M^+); 272/8 (M^+ – CH_2=C=O); 254/5 (M^+ – CH_2=C=O – H_2O); 230/48 (M^+ – 2 CH_2=C=O); 212/17 (M^+ – 2 CH_2=C=O – H_2O); 196/22, 184/37, 157/17, 153/15, 144/17, 141/20, 128/20, 116/75, 115/25, 97/17, 84/100, 83/45. – UV. (EtOH): Max. 290 (10), 272 (370), 265 (390), 218 (4680); Infl. 266 (390), 262 (370). – ^{1}H-NMR. (100 MHz, $CDCl_3$): δ = 7.6–7.1/*m*, 4 H (aromatic H's); 6,27/*d* (*J* = 6), 1 H (H–C(2)); 5,46/*d* × *d* (*J* = 3 and 10), 1 H (Hα–C(8)); 3,75/*d* × *d* (*J* = 6 and 10), 1 H (H–C(1)); 3.46/*d* × *d* × *d* × *d* (*J* = 2, 3, 5 and 5.5) 1 H (H–C(5)); 3.32/*AB* × *d* × *d* (*J* = 2, 2 and 18), 1 H (Hβ–C(4)); 3.00/*AB* × *d* × *d* (*J* = 3, 3 and 18), 1 H (Hα–C(6)); 2.87/*AB* × *d* (*J* = 5.5 and 18), 1 H (Hα–C(4)); 2.45/*AB* × *d* × *d* (*J* = 2, 5 and 18), 1 H (Hβ–C(6)); 2.00/*s*, 6 H (2 × OAc). Spin-decoupling experiments: Irradiation at δ = 6.27 ppm (H–C(2)) converted the signal at δ = 3.75 ppm (H–C(1)) to *d* (*J* = 10); irradiation at δ = 5.46 ppm (Hα–C(8)) converted the signal at δ = 3.75 ppm (H–C(1)) to *d* (*J* = 6) and the signal at δ = 3.00 ppm (Hα–C(6)) to *d* × *d* (*J* = 3 and 18); irradiation at δ = 3.00 ppm (Hα–C(6)) converted the signal at δ = 5.46 ppm (Hα–C(8)) to *d* (*J* = 10).

$C_{18}H_{18}O_5$ (314.32) Calc. C 68.78 H 5.77% Found C 69.02 H 5.88%

When the reduction was repeated with 0.2 g (0.95 mmol) of **6** in 15 ml of freshly distilled acetic anhydride the chromatographic purification yielded two fractions. The first consisted of 0.1 g (33%) of the bicyclic *diacetoxy-enone* **10** (^{1}H-NMR.-spectrum identical with the one described above). The second chromatography fraction gave 0.13 g (45%) of a compound with the following properties: m.p. 115–130° (sublimes at 98–100°/0.1 Torr). – IR. ($CHCl_3$): 3060*w*, 3030*w*, 3005*w*, 2940*w*, 2850*w*, 1730*s* (C=O), 1450*m*, 1370*s*, 1260*s*, 1240–1200*s*, 1088*s*, 1025*m*. – MS. 300/16

(M^+); 240/72 ($M^+ - CH_3CO_2H$); 198/60 ($M^+ - CH_3CO_2H - CH_2=C=O$); 180/44 ($M^+ - 2\,CH_3CO_2H$); 158/20; 157/76; 141/15; 129/28; 128/27; 115/19; 43/100. – ^{1}H-NMR. (100 MHz, $CDCl_3$): δ = 7.12/*s* on top of 7.4–6.9/*m*, 4 H (aromatic H's); 3.4–3.1/*m*, 2 H (H–C(3), H–C(7)); 3.0–2.3/*m*, 8 H (H–C(1), H–C(2), H–C(5), H–C(8), 2×H–C(4), 2×H–C(6)); 2.10/*s* and 2.08/*s*, together 6 H with intensity ratio ~3:1 (2×OAc).

$C_{18}H_{20}O_4$ (300.36) Calc. C 71.98 H 6.71% Found C 71.46 H 6.76%

It is possible that this product is a mixture of diastereomers of *3,7-diacetoxy-9,10-benzo-tricyclo[3.3.2.0^{2,8}]dec-9-ene* (**11**).

When the reduction was repeated with acetic anhydride, which had been freshly distilled over sodium acetate, crystallization of the crude product yielded 50% of *9,10-benzo-tricyclo[3.3.2.0^{2,8}]-dec-9-ene-3,7-dione* (**3**) whose m.p., mass- and ^{1}H-NMR.-spectra were identical with those described in section 2.1. for the *tricyclic dione* **3**. The ^{1}H-NMR. spectrum of the crude product showed no signals belonging to either of the two products isolated in the preceding experiments of this section.

In another experiment the reduction led to a mixture of the three products **3**, **10** and **11**. The chromatographic separation yielded 14% of the *tricyclic diketone* **3**, 29% of the *bicyclic diacetoxy-enone* **10** and about 35% of a 1:1 mixture (from ^{1}H-NMR. spectrum) of the *bicyclic diacetoxy-enone* **10** and the *diacetate* (possibly **11**).

3. Enol-acetates from 9,10-benzo-tricyclo[3.3.2.0^{2,8}]dec-9-ene-3,7-dione (3). – A solution of 50 mg (2.4 mmol) of **3** and 20 mg of *p*-toluene sulfonic acid in 5 ml of isopropenyl acetate was heated under reflux for 24 h. During the last 4 h the volume of the solution was allowed to diminish to about 3 ml by evaporation. Water was added and the mixture extracted with $CHCl_3$. The extracts were washed with 5% aqueous $NaHCO_3$, dried and evaporated to leave a brown oil. On addition of ether a precipitate formed which was filtered, washed with ether and dried to leave 33 mg (47%) of *3,7-diacetoxy-9,10-benzo-tricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene* (**4**) (*3,7-diacetoxy-benzo-bullvalene*), m.p. 160–165°. Recrystallization from chloroform/hexane raised the m.p. to 166.5–168.5°. – IR. ($CHCl_3$): 3040–3010*w*, 1758*s* (OAc); 1678*w* (C=C–OAc); 1496*m*, 1457*w*, 1401*w*, 1372*s*, 1235–1195*m*, 1158*w*, 1125*m*, 1101*s*, 1020–1010*w*, 913*w*. – IR. (KBr): 3040*w*, 3025*w*, 1760*s* (OAc), 1667*m* (C=C–OAc), 1499*m*, 1459*w*, 1400*w*, 1372*s*, 1210*s*, 1155*w*, 1125*m*, 1109*s*, 1100*s*, 1090*m*, 1015*m*, 910*m*, 832*m*, 795*w*, 781*w*, 770*m*, 741*w*, 722*m*, 710*w*, 688*w*. – MS. 296/1 (M^+); 254/10 ($M^+ - CH_2=C=O$); 236/*s* ($M^+ - CH_2=C=O - H_2O$); 212/25 ($M^+ - 2\,CH_2=C=O$); 194/71 ($M^+ - 2\,CH_2=C=O - H_2O$); 165/30; 152/15; 128/18; 43/100. – ^{1}H-NMR. (100 MHz, $CDCl_3$): *At RT.*: δ = 7.15/br. *s*, 4 H (aromatic H's); 6.1–4.9/br. *s*, 2 H (H–C(4), H–C(6)); 3.8–2.2/*m*, 4 H (H–C(1), H–C(2), H–C(5), H–C(8)); 2.06/*s*, 6 H (2×OAc). *At −25° to −10°*: δ = 7.6–6.8/*m*, 4 H (aromatic H's); 5.70/*d* (J = 10), 2 H (H–C(4), H–C(6)); 3.52/*t* (J = 10), 1 H (H–C(5)); 3.00/*t* (J = 8), 1 H (H–C(1)); 2.50/*d* (J = 8), 2 H (H–C(2), H–C(8); 2.14/*s*, 6 H (2×OAc). *at 60°*: δ = 7.14/br. *s*, 4 H (aromatic H's); 6.0–2.2/br. signal due to equilibrating H–C(4), H–C(6) and H–C(2), H–C(8); 3.18/br. *t* (J = 8) due to equilibrating H–C(1) and H–C(5); 2.08/*s*, 6 H (2×OAc).

$C_{18}H_{16}O_4$ (296.326) Calc. C 72.96 H 5.44% Found C 72.53 H 5.77%

In another experiment a solution of 25 mg (1.2 mmol) of **3** and 5 mg of *p*-toluene sulfonic acid in 3 ml of isopropenyl acetate was heated under reflux for 16 h without allowing the volume of the solution to diminish. Work-up as described above gave an oil which was purified by preparative TLC. on silica gel with chloroform/acetone 9:1 to yield 27 mg of a semisolid whose ^{1}H-NMR. spectrum indicated it to be mostly a 2:1 mixture of educt **3** and another compound. Crystallization from chloroform/hexane gave 5 mg (20%) of recovered **3** and 5 mg (17%) of slightly impure *3-acetoxy-9,10-benzo-tricyclo[3.3.2.0^{2,8}]deca-3,9-diene-7-one* (**9**) as white needles, m.p. 180–184°. – IR. ($CHCl_3$): 3030–3005*w*, 1760*s* (OAc), 1680*s* (C=O), 1495*m*, 1360*m*, 1230–1193*m*, 1120*s*, 1108*m*, 1090*m*, 945*w*. – MS. 254/5 (M^+); 226/4 ($M^+ - CO$); 212/42 ($M^+ - CH_2=C=O$); 194/10 ($M^+ - CH_2=C=O - H_2O$); 184/61 ($M^+ - CH_2=C=O - CO$); 170/56, 169/33, 155/16, 153/25, 152/20, 142/33, 141/61, 139/17, 129/30, 128/61, 127/20, 116/72, 115/31, 43/100. – ^{1}H-NMR. (100 MHz, $CDCl_3$): δ = 7.5–6.9/*m*, 4 H (aromatic H's); 5.77/*d*×*d* (J = 3 and 10), 1 H (H–C(4)); 3.32/*d*×*t* (J = 10 and 4), 1 H (H–C(5)); 2.9–2.3/*m* with a quartet-like signal at 2.82 (splitting ~4) and a triplet-like signal at 2.64 (splitting ~4), 5 H (H–C(1), H–C(2), H–C(8), 2×H–C(6)); 2.06/*s*, 3 H (OAc).

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81. Rastronole A, B, C, D, E, F, G und H; eine Gruppe multioxygenierter Diterpenbitterstoffe der *ent*-Kauran-Reihe aus *Englerastrum scandens* ALSTON

von **Kyosuke Nomoto, Peter Rüedi** und **Conrad Hans Eugster**

Organisch-chemisches Institut der Universität Zürich, Rämistrasse 76, CH-8001 Zürich

Herrn Prof. Dr. *Tsunematsu Takemoto*, Tohoku Universität, Sendai, Japan, gewidmet

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Rastronols A, B, C, D, E, F, G, and H, a group of multioxygenated bitter principles with *ent*-kaur-16-en-15-one structure from *Englerastrum scandens* ALSTON (*Labiatae*). – *Summary.* We have isolated from the leaves of *Englerastrum scandens* from Kenya eight new, highly oxygenated *ent*-kaur-16-en-15-ones named rastronol A, B, C, D, E, F, G, and H, and determined their structures mainly by spectroscopic techniques as **1**, **8**, **14**, **17**, **20**, **29**, **39**, and **51** respectively.

1. Einleitung. – Bei der Überprüfung von neuen ostafrikanischen Labiaten auf das Vorkommen von diterpenoiden Chinonen und Hydrochinonen[1]) fiel uns *Englerastrum scandens* ALSTON[2]) wegen der intensiven Bitterkeit seiner Blätter und Zweige auf. Durch Digerieren von getrockneten Blättern und Zweigen mit Äther und Chromatographie des Extraktes an Kieselgel konnten acht einheitliche Stoffe isoliert und kristallisiert werden. Wir nennen sie *Rastronole* (vergleiche Tabelle 1 und *Schema 1*). Unsere Untersuchungen haben, wie nachfolgend abgeleitet wird, zu den in *Schema 1* aufgeführten Strukturen geführt. Davon sind die Paare **8** und **14**, **17** und **20** sowie **39** und **51** miteinander durch chemische Reaktionen verknüpft worden. Eine direkte Korrelation mit dem Grundkörper *ent*-Kauran oder einem seiner Derivate wurde

[1]) Coleone und Royleanone; vergleiche [1] und darin zitierte frühere Arbeiten.

[2]) Früher *Coleus scandens* GÜRKE, eine perennierende, kriechende oder klimmende Staude mit fleischigen Blättern und Zweigen, ist in SO-Kenya (Nairobi, Embu, Machakos) an Flussrändern und felsigen Stellen des *Combretum*-Buschgebietes nicht häufig zu finden. Die Pflanze steht dem Genus *Plectranthus* nahe. Dr. *P. R. O. Bally*, Nairobi, hatte uns auf diese Pflanze aufmerksam gemacht. Sie wird in der Städtischen Sukkulentensammlung Zürich in Kultur gehalten.