Acid-catalyzed interconversion of the C(8′) epimeric photoproducts **9** and **10**, transformation of both compounds to the same keto-γ-lactone, and the IR., NMR., and mass spectrometric data provide strong support for the constitution of **9** and **10**. The full molecular structure was determined by an X-ray diffraction analysis of **9**. The crystals are monoclinic (a = 7.682, b = 14.448, c = 12.925 Å, β = 108.4°), space group P 2_1/c, with four molecules in the unit cell. Intensity measurements of 1277 reflections were carried out with a *Philips* PW 1100 automatic 4-circle diffractometer with MoKα radiation. Phases were determined by direct methods, and a first *Fourier* synthesis yielded a consistent and well resolved image of the molecule with all atoms present. The positions of all the hydrogen atoms were unambiguously obtained from a difference synthesis at a later stage of the analysis. The final R factor, based on 991 reflections, is 0.049.

Financial support for this work by the *Fonds National Suisse de la Recherche Scientifique* and by *Firmenich & Cie*, Geneva, is gratefully acknowledged.

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[2] *Cf. D. Valentine, N. J. Turro & G. S. Hammond*, J. Amer. chem. Soc. *86*, 5202 (1964).

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260. Triasteranetrione

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(5. IX. 73)

Zusammenfassung. Eine Synthese von Bicyclo[3.3.1]nonan-3,7,9-trion-9-(äthylen)acetal (**6**) durch doppelte *Michael*-Addition von Aceton-dicarbonsäure-dimethylester (**9**) an Benzochinon-mono(äthylen)acetal (**8**) und anschliessende Verseifung und Decarboxylierung des intermediären 2,4-Dicarbomethoxy-bicyclo[3.3.1]nonan-3,7,9-trion-9-(äthylen)acetals (**10**) wird beschrieben. Bromierung des Triketon-monoacetals **6** mit Brom in Eisessig liefert 2α,4β,6α,8β-Tetrabrom-bicyclo[3.3.1]nonan-3,7,9-trion-9-(äthylen)acetal (**12**), dessen Konfiguration sich aus dem NMR.-Spektrum mit Hilfe von Symmetrieargumenten und aus Vergleichen von chemischen Verschiebungen ergibt. Durch Behandlung des rohen Tetrabromids (**12**) mit Triäthylamin entsteht ein Gemisch von 2,4-Dibrom- (**13**) und 2,6-Dibrom-triasteran-3,7,9-trion-9-(äthylen)acetal (**14**), welches sich einerseits mit Säure zu einem 1:2-Gemisch von 2,4-Dibrom- (**15**) und 2,6-Dibrom-triasteran-3,7,9-trion (**16**) hydrolysieren und andererseits mit Tri-*n*-butyl-zinnhydrid zu Triasteran-3,7,9-trion-9-(äthylen)acetal (**17**) reduktiv debromieren lässt. Hydrolyse des Triketon-monoacetals (**17**) oder reduktive Debromierung des Triketodibromid-Gemisches (**15** und **16**) führt zum hochschmelzenden, in den meisten Lösungsmitteln wenig löslichen Triasteran-3,7,9-trion (**4**). Die Spektraleigenschaften der erwähnten Substanzen werden diskutiert und zur Bestätigung der Strukturen zugezogen.

1. Introduction.

– The triasterane skeleton (**1**) is of particular interest inasmuch as all six cyclopropyl-methylene bridge bonds ideally 'bisect' [1] a cyclopropane ring. The orbitals of any trigonal bridge carbon atoms are thus favorably disposed for

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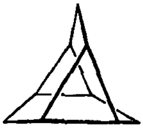
'through bond' [2] interaction. In this system there might also be a 'through space' [2] interaction, which has been discussed under the title of bicycloaromaticity [3]. Of interest for a study of such interactions could be the three triasteranones. The preparation of triasteranone (**2**) and triasteranedione (**3**) have been reported previously [4–5]. This work is concerned with the synthesis of triasteranetrione (**4**).



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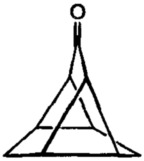

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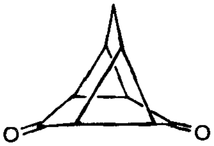

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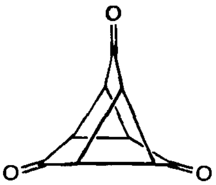

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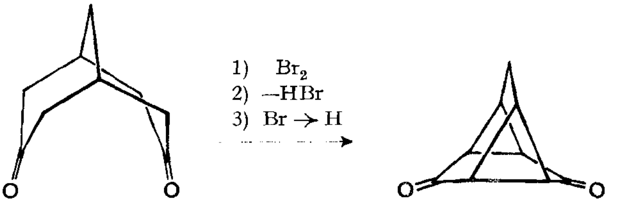
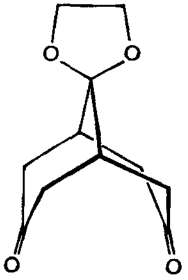
A route to triasteranetrione (**4**) from the bicyclic acetal dione **6**, employing the conditions found suitable in the synthesis of triasteranedione (**3**) from bicyclo[3.3.1]-nonane-3,7-dione (**5**) [5], offered a promising approach. However, the required bicyclo [3.3.1] nonane-3,7,9-trione-9-(ethylene)acetal (**6**) has not previously been synthesized.



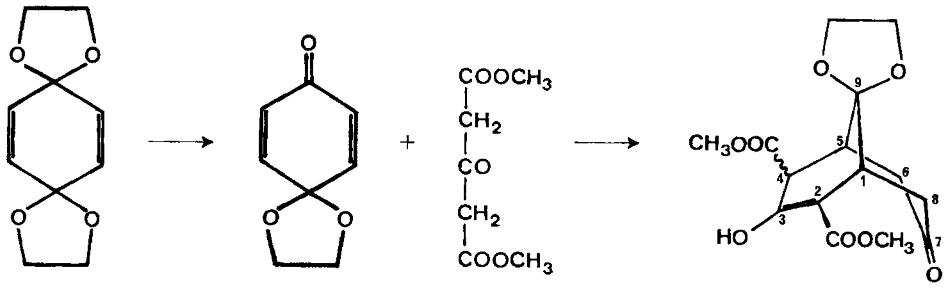
5 **3**



6

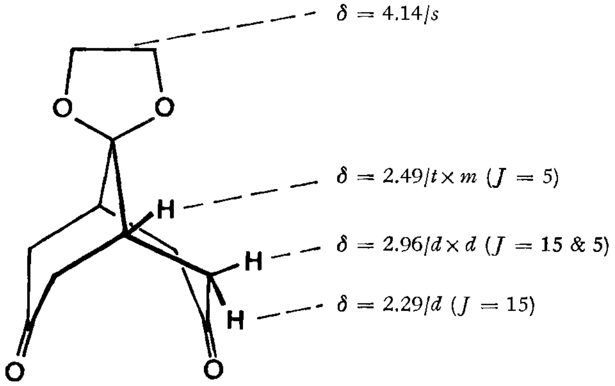
2. Synthesis of bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal (6). – Benzoquinone-mono(ethylene)acetal (**8**), recently prepared [6] by the partial hydrolysis of benzoquinone-bis(ethylene)acetal (**7**), was treated with one mol-equivalent of acetone-dicarboxylic-acid dimethylester (**9**) and a catalytic amount of sodium ethoxide. Two consecutive *Michael* condensations occurred, the first intermolecular and the second intramolecular, to yield 86% of 2,4-dicarbomethoxy-bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal (**10**) as a mixture of stereomers. This approach has previously been used [7] with 4,4-dialkyl-cyclohexa-1,4-dien-3-ones to construct the 9,9-dialkyl-bicyclo[3.3.1]nonane skeleton.

In the NMR.-spectrum of **10** the three closely situated singlets at $\delta = 3.76$, 3.75 and 3.74 ppm may be assigned to three $COOCH_3$-groups, but their relative intensities can – due to their closeness – not be evaluated. The two singlets at $\delta = 12.13$ and 12.03 ppm in the ratio of 3:1 as well as the intensity relation of these signals with the rest of the NMR.-spectrum are consistent with the interpretation that the *Michael* adduct contains two fully enolized stereomers of **10** in the ratio of 3:1. Without further purification this mixture was hydrolyzed under basic conditions and decarboxylated to yield 60–70% of bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal (**6**), m.p. 138°. In one experiment, 9% of a second product, m.p. 145°, (partially hydrolyzed and decarboxylated) was also isolated; it will be described further below.



7 **8** **9** **10**

The NMR.-spectrum supports the contention that bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal prefers the twin chair conformation, which is shown in formula **6**, for the following reason:



6

The two four-proton signals at $\delta = 2.96$ and 2.29 ppm must be assigned to the two types of protons next to the carbonyl groups, namely H–C(2), H–C(4), H–C(6) and H–C(8)[2]. The fact that there are only two such signals means that the two six-

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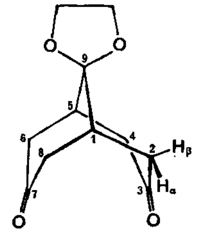
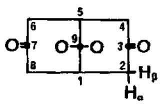
[2] In the present discussion we use the following formulae, numbering and configurational symbols:



perspective formula



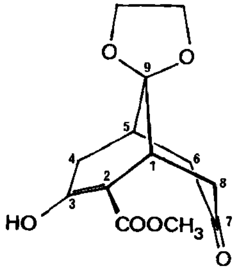
projection formula

membered rings must have the same conformation. The fairly large difference in chemical shifts of these two groups of equivalent protons fits better for the chair conformation of both cyclohexanones since the four protons in the β-configuration²) then would be axial and experience considerable deshielding ($\delta = 2.96$ ppm), due to their greater proximity to the acetal O-atoms, as compared to the four equatorial α-protons ($\delta = 2.29$ ppm).

Furthermore, the fact that an additional coupling of $J = 5$ Hz (aside from the geminal coupling of 15 Hz) is visible only in the $\delta = 2.96$ ppm signal (H_β) means that the two cyclohexanone rings cannot populate a twist-boat family, because the torsional motion within that family encompasses a multiple and by compensation symmetrical wagging of the α-protons²) across a *syn-periplanar* position relative to the angular protons. The signal with the 5 Hz vicinal coupling (2.96 ppm) would then have to be assigned of the α-protons², but the β-protons, in that case, could not show a vicinal coupling of zero. The observed coupling difference must be due to slight distortion (flattening) from the ideal chair (as was also observed in other compounds with this skeleton [8]). Such a distortion can only decrease the torsional angle of H_β with a bridgehead hydrogen (bringing it closer to 30°) and increase that of H_α (bringing it closer to 90°).

The observed shielding difference between the α- and β-type protons is due to two effects: a) The above mentioned difference in proximity to an acetal oxygen atom and b) the difference in position (equatorial minus axial) relative to a carbonyl group³). The combination of the two effects gives $\Delta\delta_{\alpha-\beta} = -0.67$ ppm. This value will be used in another conformational argument below.

The second product from the hydrolysis and decarboxylation reaction, m.p. 145°, was shown to be the fully enolized 2-carbomethoxy-bicyclo[3.3.1]nonane-3,7,9-



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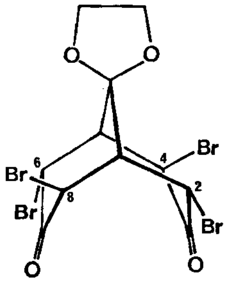
[3]) The NMR.-spectrum of bicyclo[3.3.1]nonane-3,7-dione (**5**) (see Exper. Part) shows the signal of the β-protons²) at 2.63 as a $d \times d$ ($J = 15$ and 5) and that of the α-protons at 2.35 ppm as a slightly broadened *d* ($J = 15$). It has been suggested [9], on the basis of the carbonyl absorption in the IR.-spectrum, that **5** prefers the twin chair conformation. (This is in accord with conclusions [8] about other bicyclo[3.3.1]nonane systems, where the twin chair conformation should be even less favored.) The vicinal coupling of 5 Hz found in one but not the other of these signals also suggests, as argued above for the diketone **6**, a preferred twin-chair conformation. The vicinal coupling of 5 Hz identifies the 2.63 ppm signal as belonging to the β-protons, since the chairs are flattened. Effect b, in this case, is $\Delta\delta_{\alpha-\beta} = -0.28$ ppm (compare [10]). Effect a, observed in **6**, must be about -0.4 ppm.

trione-9-(ethylene)acetal (**11**) on the basis of an elemental analysis ($C_{13}H_{16}O_6$), the mass spectrum (*m/e* 268) and the NMR.-spectrum (singlet at $\delta = 12.08$ ppm and appropriate intensity ratio of the other signals).

3. Synthesis of triasteranetrione (4). – The synthesis of triasteranetrione (**4**) from bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal (**6**) essentially follows the procedure used for the synthesis of triasteranedione (**3**), with the sole exception that an acetal hydrolysis is incorporated at one of two stages in the process.

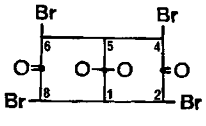
When **6** was treated with 4 mol-equivalents of bromine in acetic acid a 30% yield of 2α,4β,6α,8β-tetrabromo-bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal (**12**)2)), m.p. 241°, was precipitated directly from the reaction mixture. Elemental analysis confirms the composition $C_{11}H_{10}Br_4O_4$, especially the presence of four bromine atoms, even though no corresponding molecular ion is observed in the mass spectrum. The fact that the peaks of highest *m/e* values (443, 445, 447, 449, showing the presence of three bromine atoms) are odd, characterizes them as fragment ions.



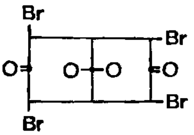
12

An apparent anomaly in the mass spectrum, namely the appearance of peaks at *m/e* 283, 285, 287 in the ratio of 1:2:1, can be understood when it is considered that the molecular ion, after losing one bromine atom, can split off either two more bromine atoms (giving *m/e* 285, 287) or two hydrogen bromide molecules (giving *m/e* 283, 285).

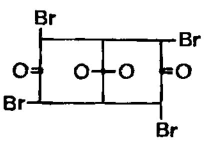
The assignment of configuration2)) to the centers carrying bromine atoms in **12** is possible from the following interpretation of the NMR.-spectrum: The two sets of lowest field signals ($\delta = 5.66$ and 4.86 ppm) are attributed to the four H–C(Br) protons. Since these two signals are of equal intensity (2 protons each) and show interpretable coupling, there can be only two sets of pairwise equivalent H–C(Br) protons. Thus, of the seven possible stereomers of tetrabromo-bicyclo[3.3.1]nonane-3,7,9-



A (C_s)



B (C_s)



C (C_2)

trione-9-(ethylene)acetal (**12**), only those two with C_s symmetry (**A** and **B**) and the one with C_2 symmetry (**C**) need be considered.

In the NMR.-spectrum of **12**, the highest field signal (two protons), which appears as a finely structured doublet of doublets at $\delta = 3.52$ ppm ($J = 1$ and 5 Hz), must be assigned to the angular hydrogens H–C(1) and H–C(5). This eliminates isomer **A** from further consideration because its angular protons would be expected to exhibit notably different chemical shifts; for H–C(5) is in 1,3-parallel vicinity⁴) with two bromine atoms (Br–C(4) and Br–C(6)) whereas H–C(1) is in such vicinity only with two hydrogen atoms (H–C(2) and H–C(8)).

A decision between structures **B** and **C** can be made on the basis of the fairly large difference ($\Delta\delta_{\alpha-\beta} = -0.80$ ppm) in the chemical shifts of the two types of H–C(Br) protons, the pair in α- and the pair in β-configuration²). The expected effects will be discussed on a twin-chair conformation of **12**.

In both isomers (**B** and **C**) each of the 'β-type'-hydrogen atoms (in **B**: H–C(6) and H–C(8); in **C**: H–C(2) and H–C(6)) is axial next to the carbonyl group and 1,3-parallel (here *syn*-diaxial) with an acetal oxygen atom, whereas each of the 'α-type'-hydrogen atoms (in **B**: H–C(2) and H–C(4); in **C**: H–C(4) and H–C(8)) is equatorial next to the carbonyl group and away from the acetal oxygen atom. The effects expected to be contributing to the difference in chemical shifts of the H_α and H_β protons are the same as the ones observed on the diketone **6** (see above), namely $\Delta\delta_{\alpha-\beta} = -0.67$ ppm.

In isomer **C** these effects are the only ones differentiating the H_α from the H_β protons, each proton of *both* types also being under the influence of 1,3-parallel vicinity⁴) with one bromine atom. The predicted $\Delta\delta_{\alpha-\beta}$ value would, therefore, be about -0.67 ppm.

In isomer **B**, on the other hand, only the protons of one type (H_α) are under the influence of 1,3-parallel vicinity⁴) with one bromine atom each. The deshielding caused by a bromine atom in such a vicinity can be evaluated from the NMR.-spectrum of 4β,8β,9β,10α-tetrabromo-1,3-dihydroxy-2-oxa-adamantane [5] as about $+0.43$ ppm. Since this deshielding in isomer **B** does not affect the H_β protons, the predicted $\Delta\delta_{\alpha-\beta}$ value for isomer **B** is about $(-0.67 + 0.43 =)$ -0.25 ppm.

Clearly, the observed value $\Delta\delta_{\alpha-\beta} = -0.80$ ppm in the isolated isomer of 2,4,6,8-tetrabromo-bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal fits better for structure **C**. On this basis, the 2α,4β,6α,8β-configuration²) **12** is assigned to this isomer.

The reasonable correspondence of the calculated $\Delta\delta_{\alpha-\beta}$ value with the observed one offers some evidence that the assumption of a preferred twin-chair conformation for the tetrabromo-diketone **12** is correct. The spectral properties of **12** are thus interpreted as follows:

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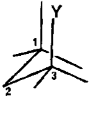
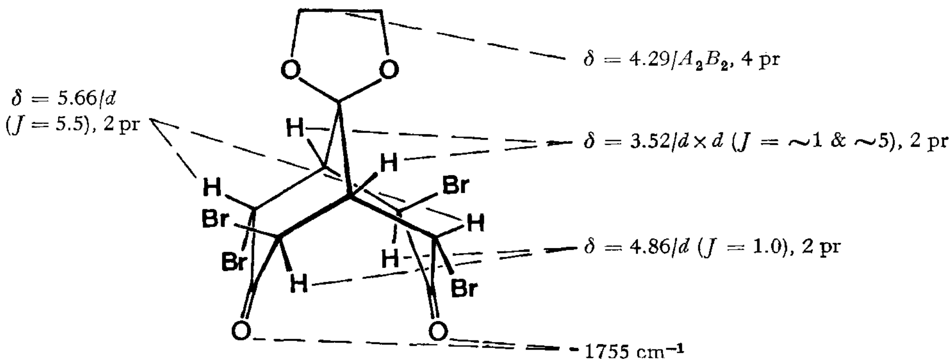
⁴) Under 1,3-parallel vicinity we understand the relative position of two atoms or groups (X and Y), if their bonds to 1,3-situated carbon atoms are roughly parallel and in the same direction, as is shown in the following diagram. In a saturated 6-membered ring this corresponds to the *syn*-diaxial vicinity.





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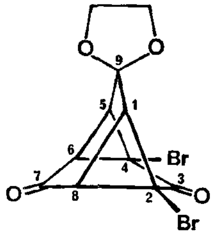
It is of possible interest that the 2,4,6,8-tetrabromo-bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal was isolated in the diketo form **12**, whereas the corresponding intermediate in the triasterane-dione (**3**) synthesis, the 2,4,6,8-tetrabromo-bicyclo[3.3.1]nonane-3,7-dione, was isolated in the hydrated 1,3-dihydroxy-2-oxa-adamantane form. It is not known whether the difference in this case is due to the use of non-aqueous working-up or to the doubly occurring 1,3-parallel[4]) (here *syn*-diaxial) vicinity of bromine and acetal oxygen atoms, which could push the carbonyl groups away from each other.

When the *crude* bromination product of **6** was treated with triethylamine a mixture of isomeric dehydrobrominated products was obtained in 57% yield. By analogy with the triasteranedione work [5], it was anticipated that these products might be 2,4-dibromo-triasterane-3,7,9-trione-9-(ethylene)acetal (**13**) and 2,6-dibromo-triasterane-3,7,9-trione-9-(ethylene)acetal (**14**). This is supported by the following properties of the mixture which, however, furnish no information on the ratio of its



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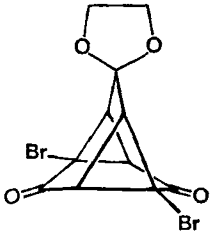

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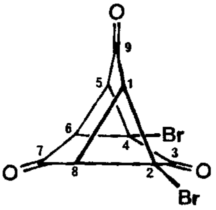
two components: 1) The mass spectrum with its isotopic molecular ions at *m/e* 362, 364, 366, 2) the elemental analysis corresponding to $C_{11}H_8Br_2O_4$, and 3) the NMR.-spectrum which contains no signals inconsistent with structures **13** and **14** and which shows an intensity ratio of 1:1 between the singlet due to the ethylene acetal protons at δ = 4.17 ppm and the multiplet at δ = 3.2–2.7 – with its sharp singlet at 2.80 ppm – due to the remaining protons.

Under reflux in dilute aqueous hydrochloric acid the isomeric mixture of **13** and **14** was quantitatively hydrolyzed to a mixture containing 2,4-dibromo-triasterane-trione (**15**) and 2,6-dibromo-triasteranetrione (**16**) in a ratio of 1:2. These structures are supported by the elemental analysis ($C_9H_4Br_2O_3$), the mass spectrum (*m/e* 322, 320, 318) of the mixture and its NMR.-spectrum, which is more informative as to the ratio of the components **15** and **16** than in the case of **13** and **14**: A singlet at $\delta = 3.69$ ppm is attributed to isomer **15** since all its (four) protons are equivalent. The *AB*-quartet at $\delta = 3.74$ ppm is assigned to isomer **16** since it contains two non-equivalent proton pairs. The intensity ratio of these signals was 1:2.



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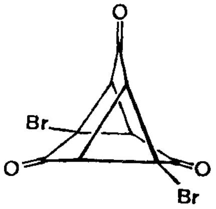

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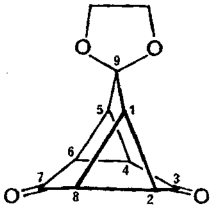
Reductive debromination of the isomeric mixture **13** and **14** with tri-*n*-butyltin hydride [11] afforded a 42% yield of triasterane-3,7,9-trione-9-(ethylene)acetal (**17**).



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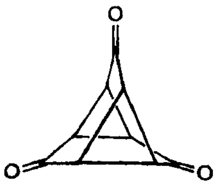
The composition of $C_{11}H_{10}O_4$ was obtained from the mass spectrum (molecular ion at *m/e* 206) and the elemental analysis, and the structural assignment received support from the NMR.-spectrum, which contains only two singlets in the ratio of 2:3. The singlet at $\delta = 4.14$ ppm is assigned to the four ethylene acetal protons and the one at 2.33 ppm to the six remaining protons H–C(1), H–C(2), H–C(4), H–C(5), H–C(6) and H–C(8). In the presence of Eu(fod)$_3$ [12], the signal at $\delta = 2.33$ ppm was shifted downfield and separated into a four-proton doublet ($J = 8$ Hz) due to H–C(2), H–C(4), H–C(6) and H–C(8) and a two-proton triplet ($J = 8$ Hz) due to H–C(1) and H–C(5).

In the case of the isomeric mixture of **15** and **16**, the reductive debromination with tri-*n*-butyltin hydride [11] was accompanied by a reduction of one or more carbonyl groups (bands due to hydroxyl group in the IR.-spectrum). When the crude



4

product was oxidized with *Jones'* reagent [13] triasteranetrione (**4**) was obtained in an overall yield of 45% from the mixture of **15** and **16**. The alternative route, the hydrolysis of the acetal **17**, afforded **4** in 94% yield.

Triasteranetrione (**4**) appears as chunky plates with a very high melting point (306°) and very low solubility in many solvents. Of interest in the IR.-spectrum are the three sharp absorptions at 3110, 3095 and 3075 cm^{-1} (the only C–H stretching frequencies, which have been assigned to the hydrogen atoms on the cyclopropane rings) and a strong absorption at 1700 cm^{-1} (carbonyl). The mass spectrum shows a molecular ion at *m/e* 162 (in accord with the composition $C_9H_6O_3$) and peaks due to three consecutive losses of CO (*m/e* 134, 106 and 78) with the base peak at *m/e* 78. The NMR.-spectrum in deuterated pyridine is simply a singlet at $\delta = 2.68$ ppm.

Our experience indicates that the route **(13 + 14) → 17 → 4** is to be preferred for synthetic purposes over the one **(13 + 14) → (15 + 16) → 4.**

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.*

Experimental Part

General. All *melting points* were taken in sealed capillary tubes with a heated oil bath apparatus; the temperatures are not corrected. The *IR.-spectra* were measured on a Perkin Elmer 21 and 421 spectrometer. They are recorded as follows (solvent or support): frequency in cm^{-1}, intensity as w = weak, m = medium and s = strong. The *mass spectra* were measured on a *CEC* 21–110B or an *Atlas* CH-5 instrument. They are recorded as follows: (energy in eV): molecular ions and/or fragment ions in *m/e* (intensities relative to base peak in %). With the exception of the molecular ions along with the bromine isotope peaks, only the peaks above *m/e* = 90 and above 5% are recorded. The *^{1}H-NMR.-spectra* were measured with an HA-100 instrument. They are recorded as follows: (frequency and solvent): chemical shifts in ppm on the δ-scale (TMS internal = 0)/ multiplicity with *s* = singlet, *d* = doublet, *t* = triplet, *AB* = *AB*-quartet and *m* = multiplet (splitting *J* in Hz), relative integration in pr units (interpretation). The assignments correspond to the numbering on the formulae in the text.

We thank the MS.-laboratory (direction Prof. *M. Hesse*) for the mass-spectra, the microlaboratory (direction *H. Frohofer*) for the elemental analyses and the IR.-spectra, and Mr. *M. Karpf* as well as the NMR.-laboratory (direction Prof. *W. v. Philipsborn*) for the NMR.-spectra.

2,4-Dicarbomethoxy-bicyclo[3.3.1]nonane-3, 7, 9-trione-9-(ethylene)acetal (**10**). To a stirred solution of 12.10 g (79.7 mmol) *p*-benzoquinone-mono(ethylene)acetal (**8**) [6] in 500 ml ethanol was added 0.18 g (7.8 mmol) sodium and then, before the sodium had completely dissolved, a solution of 13.89 g (79.7 mmol) acetone-dicarboxylic-acid dimethyl-ester (**9**) in 100 ml ethanol was added dropwise over 1 h. Towards the end of the addition a colourless solid began to precipitate. Stirring was continued for 24 h, the solvent was evaporated and the dark residue was taken into $CHCl_3$ and washed with 5% aq. HCl and then with water. Removal of the solvent left 25.78 g of a brown solid, m.p. 168–191° which, after washing with cold ethanol, afforded 22.44 g (86%) of **10**, probably in the form of a mixture of stereomers as a colorless powder, m.p. 184–191°. – MS.: 326 (18); 99 (100). – IR. ($CHCl_3$): 3045 w; 3010 w; 2970 m; 2910 w; 1730 s; 1675 s; 1630 m. – NMR. ($CDCl_3$): $\delta = 12.13, 12.03/2 \times s$ (intensity ratio = 3:1) 1 pr (enolic OH); 4.2 – 3.9/*m*, 4 pr (—OCH_2CH_2O—); 3.76, 3.75, 3.74/3 × *s* (intensity ratio cannot be evaluated), 6 pr (2 × OCH_3); 3.2 – 2.2/*m*, 7 pr (H—C(1), H—C(4), H—C(5), 2 × H—C(6), 2 × H—C(8)).

$C_{15}H_{18}O_8$ (326.29) Calc. C 55.21 H 5.56% Found C 55.03 H 5.57%

Bicyclo[3.3.1]nonane-3,7,9-trione-9-(ethylene)acetal (**6**). A solution of 29.00 g (89 mmol) **10**, 11.60 g (0.29 mol) NaOH in 500 ml methanol and 500 ml water was refluxed for 8 h, cooled, acidified with 70 ml 10% aq. HCl and stirred for 2 h until effervescence had ceased. The aqueous solution was exhaustively extracted with ethyl acetate; the organic phase was washed with water, dried and evaporated to yield 18.20 g of a partially solid, crude product. Recrystallization from ethyl acetate afforded 8.93 g (48%) **6** as colorless needles, m.p. 137–138°. – MS.: 210 (52); 182 (38); 154 (48); 126 (38); 125 (29); 113 (100); 112 (23); 99 (81). – IR. (KBr): 3000 w; 2975 w; 2955 w; 2930 m; 2910 m; 1715 s. – NMR. ($CDCl_3$): δ = 4.14/*s*, 4 pr ($-OCH_2CH_2O-$); 2.96/*d*×*d* (J = 15 and 5), 4 pr (Hβ–C(2), Hβ–C(4), Hβ–C(6), Hβ–C(8)); 2.49/*t*×*m* (broadened) (J = ~5), 2 pr (H–C(1), H–C(5)); 2.29/*d* (J = 15), 4 pr (Hα–C(2), Hα–C(4), Hα–C(6), Hα–C(8)).

$C_{11}H_{14}O_4$ (210.22) Calc. C 62,84 H 6.71% Found C 63.07 H 6.75%

The material from the mother liquor was chromatographed on a column of 200 g silica gel with benzene/$CHCl_3$ 1:1. The first substance eluted was 2.20 g (9%) *2-carbomethoxy-bicyclo[3.3.1]-nonane-3,7,9-trione-9-(ethylene)acetal* (**11**) which recrystallized from ethyl acetate as colorless plates, m.p. 144–145°. – MS.: 268 (23); 236 (5); 208 (10); 113 (5); 99 (100). – IR. (KBr): 3000 w; 2965 w; 2950 w; 2930 w; 2905 w; 2895 m; 1720 s; 1665 s; 1660 s; 1615 s. – NMR. ($CDCl_3$): δ = 12.08/*s*, 1 pr (enolic OH); 4.1–4.0/*m*, 4 pr ($-OCH_2CH_2O-$); 3.70/*s*, 3 pr (OCH_3); 3.1–2.7/*m*, 4 pr (H–C(1), Hβ–C(4), Hβ–C(6), Hβ–C(8)); 2.5–2.1/*m*, 4 pr (Hα–C(4), H–C(5), Hα–C(6), Hα–C(8)).

$C_{13}H_{16}O_6$ (268.26) Calc. C 58.20 H 6.01% Found C 58.23 H 5.61%

The second substance eluted from the column was 2.68 g (14%) more of **6**, m.p. 137–138°, bringing the total yield to 11.61 g (62%).

NMR.-spectrum of bicyclo[3.3.1]nonane-3,7-dione (**5**). The diketone **5** was prepared according to the references given in [5]. – NMR. ($CDCl_3$): δ = 3.0–2.75/*m*, 2 pr (H–C(1), H–C(5)); 2.63/*d*×*d* (J = 15 and 5), 4 pr (4×Hβ); 2.35/slightly broadened *d* (J = 15), 4 pr (4×Hα); 2.22/*s* with sym. fine structure, 2 pr (2×H–C(9)). The assignment of the 2.63 and the 2.35 ppm signals to the β- and α-protons[2]) respectively was made on the assumption of a preferred twin-chair conformation (see text on compound **6** and footnote[3])) in which the chairs are somewhat flattened, thus bringing the torsional angle of the β- with the angular protons closer to 0° and that of the α-protons closer to 90°.

2α, 4β, 6α, 8β-Tetrabromo-bicyclo[3.3.1]nonane-3, 7, 9-trione-9-(ethylene)acetal (**12**). To a stirred solution of 0.21 g (1 mmol) **6** in 5 ml acetic acid was added dropwise a solution of 0.64 g (4 mmol) Br_2 in 5 ml acetic acid. A colorless precipitate, which formed during the addition, was collected after 3 h and dried. Crystallization from ethyl acetate/petroleum ether afforded 0.16 g (30%) **12** as colorless plates, m.p. 239–241°. – MS.: No molecular peak was observed. 449 (4); 447 (11); 445 (10); 443 (4); 367 (32); 365 (51); 363 (28); 287 (43); 285 (100); 283 (60); 219 (13); 217 (14); 213 (18); 211 (17); 177 (13); 133 (16); 119 (27); 117 (25); 105 (18); 95 (13). – IR. (KBr): 2970 w; 2955 m; 2940 m; 2910 w; 1755 s. – NMR. ($CDCl_3$): δ = 5.66/*d* (J = 5.5), 2 pr (Hβ–C(2), Hβ–C(6)); 4.86/*d* (J = 1.0), 2 pr (Hα–C(4), Hα–C(8)); 4.29 A_2B_2, 4 pr ($-OCH_2CH_2O-$); 3.52/*d*×*d* with fine structure (J = ~1 and ~5), 2 pr (H–C(1), H–C(5)). – Spin-decoupling: Irradiation at 3.52 ppm converted the signals at 5.66 ppm and 4.86 ppm to singlets, and irradiation at 5.66 ppm converted the signal at 3.52 ppm to a doublet with J = 1.0.

$C_{11}H_{10}Br_4O_4$ (525.81) Calc. C 25.13 H 1.92 Br 60.60% Found C 25.70 H 1.73 Br 59.1%

The mother liquor of the above crystallization was evaporated to dryness to leave 0.29 g (54%) of a residue, m.p. 202–215°, which showed a NMR.-spectrum similar to that of a pure sample of **12**, but containing a few other signals.

2, 4-Dibromo-triasterane-3, 7, 9-trione-9-(ethylene)acetal (**13**) *and 2, 6-dibromo-triasterane-3, 7, 9-trione-9-(ethylene)acetal* (**14**). To a stirred solution of 1.05 g (5 mmol) **6** in 10 ml acetic acid was added at room temperature a solution of 3.20 g (20 mmol) bromine in 5 ml acetic acid. After 1 h, the solvent was evaporated and the almost colorless residue (2.62 g) was dissolved in 60 ml tetrahydrofuran and treated, without cooling, with a solution of 5.00 g (49 mmol) triethyl amine in 20 ml tetrahydrofuran. Stirring was continued for 1 h, the solvent was evaporated, the residue was taken up in CH_2Cl_2 and washed with 5% aq. HCl and then with water. Evaporation of the solvent afforded 1.83 g of a partially solid product which was washed with cold methanol, yielding 1.04 g (57%) of a mixture of **13** and **14** as a colorless powder, m.p. 210–255°. – MS.: 366 (2); 364 (5); 362 (3); 285 (95); 283 (100); 257 (10); 255 (11); 213 (23); 211 (24); 185 (12); 183 (11); 157 (10); 155 (9); 119 (27); 117 (26). – IR. (KBr): 3060 m; 3020 w; 3000 w; 2975 w; 2910 w; 1730 s; 1705 s. – NMR. ($CDCl_3$): δ = 4.17/s (broad), 4 pr ($-OCH_2CH_2O-$); 3.1–2.8/*m* with an intense *s* at 2.80 ppm, 4 pr (H–C(1), H–C(5), H–C(6), H–C(8) in **13**, H–C(1), H–C(4), H–C(5), H–C(8) in **14**). These spectral properties do not permit an evaluation of the relative amounts of the isomers **13** and **14** in the mixture.

$C_{11}H_8Br_2O_4$ (364.00) Calc. C 36.30 H 2.22 Br 43.91% Found C 36.12 H 2.02 Br 43.33%

2,4-Dibromo-triasteranetrione (**15**) *and 2,6-dibromo-triasteranetrione* (**16**). A mixture of 0.43 g (1.18 mmol) **13** and **14** was refluxed with 50 ml 5% aq. HCl for 24 h. Evaporation of the solvent under high vacuum at 80° yielded 0.38 g (100%) of a crude mixture of **15** and **16** as a colorless powder, m.p. 210–235°. – MS.: 322 (8); 320 (18); 318 (9); 241 (20); 239 (20); 213 (67); 211 (67); 185 (34); 183 (36); 157 (44); 155 (45); 119 (100); 117 (97). – IR. (KBr): 3070 m; 2930 w; 2855 w; 1739 s; 1732 s. – NMR. ($CDCl_3$): $\delta = 3.74/AB$-quartett (with $\Delta\delta/J = \sim 30$ Hz/$\sim$9 Hz), 2 integral units (H—C(1), H—C(5) and H—C(4), H—C(8) in **16**); 3.69/*s*, 1 integral unit (H—C(1), H—C(5), H—C(6), H—C(8) in **15**). The ratio of **15** to **16**, therefore, is 1:2.

$C_9H_4Br_2O_3$ (319.95) Calc. C 33.79 H 1.26 Br 49.95% Found C 34.17 H 1.07 Br 48.77%

Triasterane-3,7,9-trione-9-(ethylene)acetal (**17**). A mixture of 1.00 g (2.76 mmol) **13** and **14** and 1.50 g (5.15 mmol) tri-*n*-butyltin hydride [11] was heated at 100° (bath) under nitrogen for 24 h. A second portion of 1.50 g tri-*n*-butyltin hydride was added and the heating was continued for another 24 h. The reaction mixture was cooled, washed with $CHCl_3$/petroleum ether 1:1 and dried to yield 0.24 g (42%) of a colorless powder, m.p. 242–244°. Crystallization from ethyl acetate afforded 0.21 g (37%) **17** as colorless needles, m.p. 242–244°. – MS.: 206 (76); 176 (14); 149 (100); 139 (10); 124 (18); 121 (11); 119 (13); 118 (71); 107 (12); 106 (36); 105 (39); 98 (10); 95 (79); 94 (18); 93 (36); 92 (34); 91 (52); 90 (86). – IR. (KBr): 3075 w; 3065 w; 3000 w; 2970 w; 2910 w; 1698 s. – NMR. ($CDCl_3$): $\delta = 4.14/s$, 4 pr ($-OCH_2CH_2O-$); 2.33/*s*, 6 pr (H—C(1), H—C(2), H—C(4), H—C(5), H—C(6), H—C(8)). In the presence of Eu(Fod)$_3$, the signal at $\delta = 2.33$ ppm shifted downfield and split up into a more downfield doublet ($J = 8$), 4 pr (H—C(2), H—C(4), H—C(6), H—C(8)) and a more highfield triplet ($J = 8$), 2 pr (H—C(1), H—C(5)).

$C_{11}H_{10}O_4$ (206.19) Calc. C 64.07 H 4.89% Found C 64.33 H 5.18%

Triasteranetrione (**4**). a) *From the isomeric dibromo-triasteranetriones* (**15**+**16**). A mixture of 0.22 g (0.69 mmol) **15** and **16** was treated with two portions of 0.40 g (1.37 mmol) tri-*n*-butyltin hydride [11] as described above. The reaction product was washed with $CHCl_3$/petroleum ether 1:1 and dried to yield a partially solid product, which evidently contained some overreduced materials, probably alcohols. – IR. (KBr): 3480 m, 3400, 1700 s. This material was dissolved in 20 ml acetone, oxidized with 1 ml *Jones*' reagent [13], isolated in the normal way and sublimed at 0.01 Torr and 160° (bath) to give 0.05 g (45%) of a colorless powder, m.p. 303–306°. Crystallization from ethyl acetate afforded 0.04 g (36%) **4** as colorless plates, m.p. 304–306°. – MS.: 162 (73); 134 (5); 106 (15); 95 (14); 78 (100). – IR. (KBr): 3110 w; 3095 w; 3075 w; 1810 w; 1770 w; 1700 s; 1400 m; 1330 m; 1320 s; 1310 s; 1300 m; 1060 s; 1045 s; 920 m; 905 m; 880 m; 870 s. – NMR. (C_5D_5N): $\delta = 2.68/s$ (all protons).

$C_9H_6O_3$ (162.14) Calc. C 66.67 H 3.73% Found C 66.42 H 3.67%

b) *From triasterane-3,7,9-trione-9-(ethylene)acetal* (**17**). A mixture of 0.06 g (0.29 mmol) of **17** and 10 ml 5% aq. HCl was refluxed for 24 h. Evaporation of the volatile components yielded 0.05 g of a colorless powder, m.p. 303–306°. Crystallization from ethyl acetate afforded 0.045 g (95%) **4** as colorless plates, m.p. 303–306°, with spectral properties identical to the ones described above.

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261. Diterpenoid Hydroquinones from *Coleus somaliensis* (S. Moore): Coleons H, I, and K

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(3. IX. 73)

Zusammenfassung. Aus den Blättern und Stengeln von *Coleus somaliensis* (S. Moore) wurden die Diterpen-Hydrochinone H, I und K (Coleone H, I und K) isoliert und ihre Struktur aufgeklärt. Coleon H ist 3α-Acetoxy-6,11,12,14,16 (oder 17)-pentahydroxy-abieta-5,8,11,13-tetraen-7-on (**2**). Coleon I ist vermutlich das entsprechende A/B-*trans*-6,7-Diketon **5**. Coleon K ist 16,17-Diacetoxy-3α,11,12,14-tetrahydroxy-abieta-8,11,13-trien-6,7-dion (**6**). Es sind die höchst hydroxylierten Coleone, die bisher aufgefunden worden sind.

Continuing our investigation of the leaf-gland pigments of East African *Labiatae* (*Coleus, Fuerstia* and *Plectranthus* spp.)[1]) we have now isolated and characterised five new diterpenoids, three coloured, two colourless, from *Coleus somaliensis* (S. Moore)[2]). The leaf-glands of this species are rich sources of pigments (*cf.* [3]).

In this communication we present evidence for the structures of the pigments, coleons H, I, and K[3]), whilst in the following paper [4] we discuss the colourless compounds, coleons G and J.

Coleon H (yellow needles, m.p. 199°, M^+ 420, $C_{22}H_{28}O_8$) shows almost identical UV./VIS. absorption to coleon C (**1**) [5] (Table 1), and in IR. absorption differs chiefly in the presence of an aliphatic ester carbonyl band at 1725 cm^{-1} (Table 2). A singlet (3H) at δ 2.14, together with signals from a hydroxyisopropyl and three tertiary methyl groups in the NMR. spectrum indicate that coleon H is an acetoxy-coleon C having the acetoxyl substituent in ring A. The relatively narrow signal ($w_{1/2}$ = 9 Hz) for the methine proton ($\rangle$C*H*OAc) at δ 4.78 precludes axial-axial coupling as well as an axial conformation for the acetoxyl at C(2) [6].

Mild oxidation of coleon H with Ag_2O in chloroform yielded an oily, orange quinone (λ_{max} 270, 410–420 nm, ν_{max} 1669 cm^{-1}) whose NMR. spectrum shows no

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[1]) For our most recent paper on *Coleus* see [1].

[2]) The species is described in [2]. Plants from the location of the type-specimen (Ga-an Libah, Somalia) were collected by P. R. O. Bally, Nairobi, and kept in the Städtischen Sukkulentensammlung, Zürich. From cuttings of these, plants for extraction were grown in Zürich.

[3]) The compounds were named in order of elution from the initial column.