IR. (CCl_4) of XIV: 1725, 1450, 1230, 1050, 848 cm^{-1}.

Mass spectra of the fluorosulfates could not be obtained, since decomposition and polymerisation took place.

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194. The Conjugative Interaction between π-Orbitals and *Walsh-e*-Orbitals in Bullvalene and Related Systems[1])

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(30. VII. 70)

Summary. The photoelectron spectra of bullvalene (**1**), dihydrobullvalene (**2**), tetrahydrobullvalene (**3**), hexahydrobullvalene (**4**), and homotropylidene (**5**) have been recorded. The first bands in these spectra are correlated with orbitals which are linear combinations of the *Walsh-e*-orbitals and of the olefinic π-orbitals. This assignment is based on a qualitative ZDO-molecular orbital model as well as on the results of extended *Hückel* calculations. As anticipated, a large interaction is found between the π- and the *Walsh-e*-orbitals in **1**, **2**, and **3**, indicative of a resonance integral $\beta \approx -2$ eV, *i.e.* of the same order as that between the two double bond π-orbitals in butadiene ($\beta = -2.4$ eV). In **5** the interaction between π- and *Walsh-e*- orbitals is negligible.

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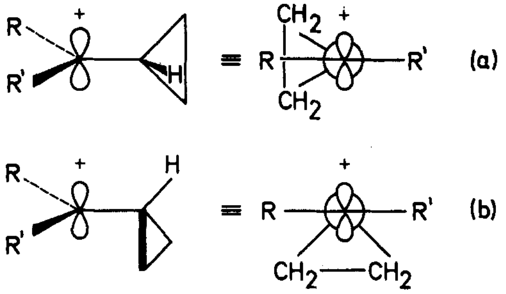
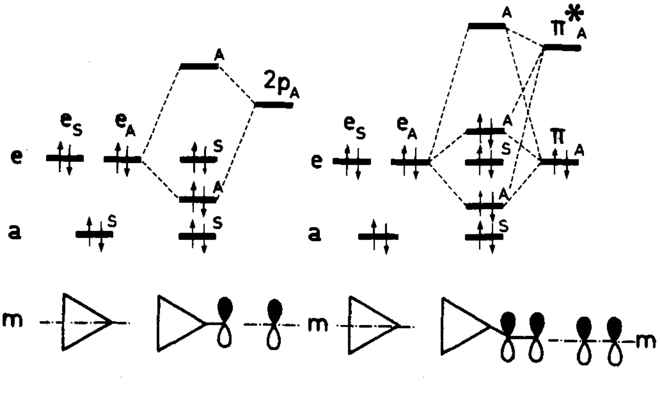
1) Part 14 of 'Applications of Photoelectron-Spectroscopy'. Part 13: [1].

Many experiments have proved the existence of a sizeable interaction between the cyclopropyl group and the α-positioned *p*-center in cyclopropyl-carbonium ions. Evidence from NMR. spectra [2] strongly suggests that the 'bisected' conformation (a) is more stable than the 'perpendicular' one (b).



This has also been confirmed, both by NMR. [3] and by electron diffraction [4] studies, for neutral systems in which a cyclopropyl group is directly connected to a π-system. Evidence derived from electronic spectra is also in general agreement with (a) being the preferred conformation [5]. The preference for conformation (a) is ascribed to an increased electron delocalization relative to that prevailing in (b), as shown in the following molecular orbital diagrams (c) and (d). On the left side of each diagram are given the three *Walsh* orbitals [6] of the cyclopropane unit. The orbital $\mathbf{e}_S$ is symmetric, $\mathbf{e}_A$ antisymmetric with respect to the plane of symmetry m (cf. equations (2), later in the text). On the right side of each diagram are shown the *p*-orbital (c) or the π-orbitals (d) which interact with the *Walsh* orbital $\mathbf{e}_A$ of the cyclopropane moiety, if the conformation of the compound system is that corresponding to (a).



(c) (d)

In case (c) the gain in energy is due to the lowering of the energy of the filled linear combination of symmetry behaviour A, *i.e.* that which is antisymmetric with respect to m. In case (d) the discrimination between the conformations (a) and (b) is less clearcut, even though (a) should still be preferred: There are now two filled orbitals of

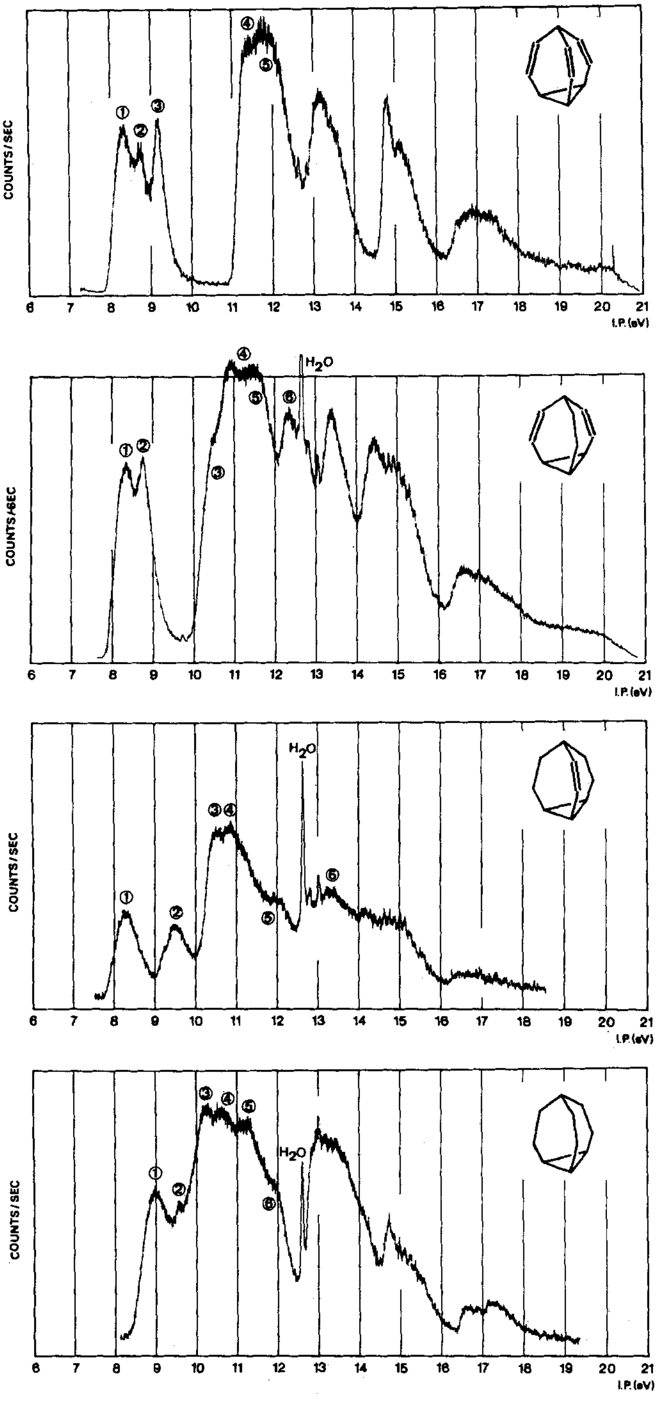
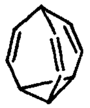


Fig. 1.
PE. spectra of bullvalene (**1**), *dihydrobullvalene* (**2**), *tetrahydrobullvalene* (**3**), *and hexahydrobullvalene* (**4**)

Abscissa:
ionisation potential in eV.
Ordinate:
intensity in arbitrary units (see experimental section). The numbering of the bands refers to that given in the table. The sharp bands labeled H_2O are due to traces of water in the sample. Sample **3** was impure (see experimental section).

symmetry behaviour A ($\mathbf{e}_A$ and π), so that the destabilization of the upper linear combination cancels to first order the stabilization of the lower one. However, the interaction with the empty antibonding orbital π^* of symmetry behaviour A will result in a second order stabilization, which will make conformation (a) again the preferred one. In contrast to the case of cyclopropyl carbonium ions, the energy difference between (a) and (b) will be rather small, and in many cases steric effects can overcome the electronic effect.

The experiments carried out so far have yielded only indirect and rather crude information concerning the absolute size of the interaction between *Walsh-e*-orbitals and *p*- and/or π-orbitals. The situation is rather similar to that encountered in the case of homoconjugation and homoaromaticity [1]. Again photoelectron spectroscopy is the method of choice for a direct measurement of the interaction, and an ideal set of test compounds is provided by the series consisting of bullvalene (**1**) [7], dihydrobullvalene (**2**) [7], tetrahydrobullvalene (**3**) [8], hexahydrobullvalene (**4**) [7], and homotropylidene (**5**) [9]. In **1** to **3** the double bonds assume the bisected conformation (a) relative to the three-membered ring, so that a large interaction between their π-orbitals and the cyclopropane-*Walsh-e*-orbitals is expected. In **5** the cyclopropane ring and double bonds are in the perpendicular conformation (b), and thus their interaction should be negligible.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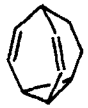
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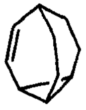
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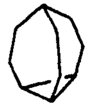
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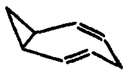
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The photoelectron spectra (PE. spectra) of **1** to **5** are shown in fig. 1 and 2. The relevant data have been collected in the table below.

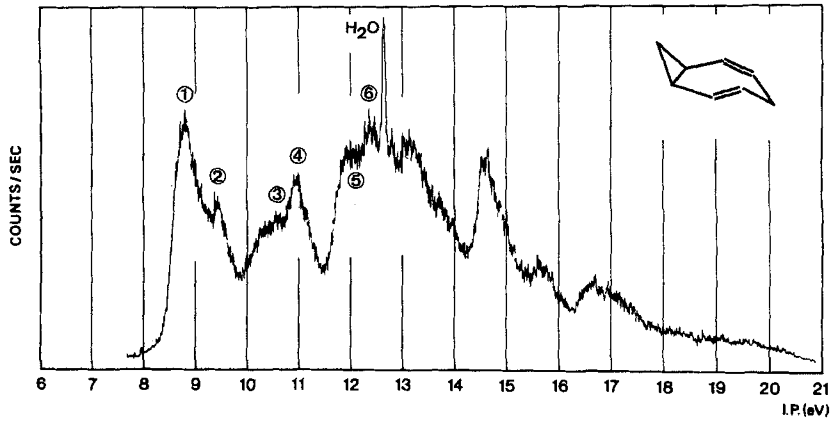


Fig. 2. *PE. spectrum of homotropylidene* (**5**) (see legend to fig. 1)

The following qualitative discussion is carried out in terms of first and second order perturbation arguments, based on a simplified molecular orbital model. The conclusions are checked by calculations using the extended *Hückel* theory of *Hoffmann* [10], and the results so obtained are in essential agreement with those derived qualitatively.

Ionisation potentials

All values are in eV. The numbering refers to that given in fig. 1, 2 and 5. a = adiabatic, v = vertical

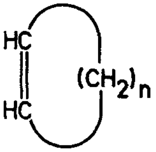
Compound	Ionisation Potentials (eV)											
	1		**2**		**3**		**4**		**5**		**6**	
	a	v	a	v	a	v	a	v	a	v	a	v
1: Bullvalene	8.05	8.34	–	8.7	9.03	9.2	11.10	11.4	–	11.7	–	–
2: Dihydrobullvalene	8.02	8.32	8.43	8.73	10.15	10.4	–	10.9	–	11.4	–	12.3
3: Tetrahydrobullvalene*)	7.95	8.26	9.14	9.50	10.19	10.5	–	10.9	–	11.9	–	13.2
4: Hexahydrobullvalene	8.71	9.05	–	9.62	–	10.25	–	10.7	–	11.1	–	11.9
5: Homotropylidene	8.43	8.79	–	9.46	10.00	10.5	–	10.9	11.68	12.0	–	12.4

*) The sample used was contaminated with **4** and another unknown compound.

All ionisation potentials (I) referred to in the discussion correspond to band maxima in the PE. spectra, *i.e.* to vertical ionisation. The reasons for this convention are twofold: Firstly these ionisation potentials are much easier to determine than those corresponding to adiabatic ionisation, especially when one is dealing with strongly overlapping bands. Secondly, assuming the validity of *Koopmans*'s theorem [11], they correspond, according to (1), to the orbital energies ε obtained from our model calculations:

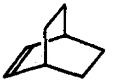
$$\varepsilon = -I \tag{1}$$

π-Orbitals. – The ionisation potential of ethylene is 10.5 eV [12] [13] [14], of propene 9.7 eV [12] [14] [15], and that of *cis*- or *trans*-2-butene 9.1 eV [12] [14] [16]. We conclude that substitution by an sp^3-hybridized carbon atom shifts the orbital energy $\varepsilon(\pi)$ of the bonding C=C π-orbital by 0.7 to 0.8 eV towards higher energies. This is in agreement with the results obtained for the higher cycloalkenes and for bicycloalkenes:



n	= 3	4	5	6	8
I	= 9.2	9.1	9.0	9.0	9.0 eV
Ref.	= [14] [17] [18]	[17] [18]	[18]	[18]	[18]

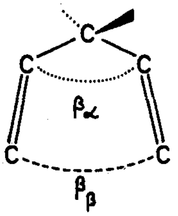
I = 9.0 eV
[19] [20]



I = 9.1 eV
[19] [20]

(The values given in [17] refer to adiabatic ionisation potentials, which agree inside the limit of errors with those found by us. They are lower by one vibrational quantum (~0.16 to 0.17 eV) than the vertical ionisation potentials used here.)

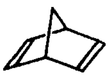
Two C=C double bonds separated by an sp^3-hybridized carbon atom will interact mainly according to two mechanisms [21]:



a) *Through-space interaction.* To a first approximation this interaction, which is overlap-controlled, is the one properly described as 'homoconjugation'. It can be parametrized by specifying the two resonance integrals β_α and β_β (see [1] and [17]).

b) *Through-bond interactions.* With reference to a simple molecular orbital model, these interactions may be classified into two types: (a) hyperconjugation through the locally antisymmetric linear combination of the C–H σ-orbitals of the connecting sp^3-C-atom and (b) interaction with other σ-bonds in the molecule. Note that these interactions are strongly symmetry controlled. (For the sake of convenience, the effect of these interactions can be absorbed in a formal way into the parameters β_α and β_β.)

From the PE. spectra of norbornadiene (**6**) and bicyclo[2.2.2]octadiene (**7**) the following values are obtained: $\beta_\alpha = \beta_\beta = 0.4$ eV for **6**; $= 0.3$ eV for **7**. Theory predicts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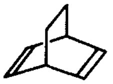
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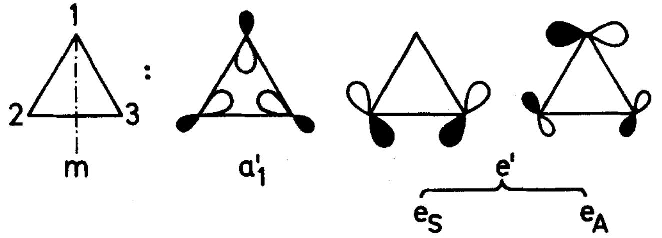
8


9

that in both cases the situation is dominated by the through-space interaction (homoconjugation) and that the antisymmetric linear combination $\mathbf{b}_2(\pi)$ of the two π-orbitals lies above the symmetric one $\mathbf{a}_1(\pi)$. However, through-bond interaction tends to decrease the orbital gap between $\varepsilon(\mathbf{b}_2(\pi))$ and $\varepsilon(\mathbf{a}_1(\pi))$ [1] [20] [21], so that the β-values quoted above are lower limits for pure through-space interaction.

A final effect to be mentioned is that the simultaneous presence of two double bonds in a hydrocarbon (such as in **6** and **7**) tends to shift the mean $\overline{\varepsilon(\pi)} = (\varepsilon(\mathbf{a}_1(\pi)) + \varepsilon(\mathbf{b}_2(\pi)))/2$ of the π-orbital energies by -0.1 to -0.2 eV towards lower energies, relative to the orbital energy $\varepsilon(\pi)$ of a single π-orbital.

***Walsh*-Orbitals.** – According to *Walsh* [6] the CC σ-orbitals of cyclopropane (D_{3h}) are best represented as follows:



We shall be concerned only with the top bonding degenerate pair $\mathbf{e}'$, which in zero differential overlap approximation (ZDO) can be written as

$$\mathbf{e}' \begin{cases} \mathbf{e}_S = \dfrac{1}{\sqrt{2}}\,(2\mathbf{p}_2 - 2\mathbf{p}_3) \\[2ex] \mathbf{e}_A = \dfrac{1}{\sqrt{6}}\,(2\cdot 2\mathbf{p}_1 - 2\mathbf{p}_2 - 2\mathbf{p}_3)\,. \end{cases} \qquad (2)$$

The orbital $\mathbf{e}_S$ is symmetric, $\mathbf{e}_A$ antisymmetric with respect to a reflection in the plane passing through atom 1 and bisecting the bond 2–3.

Basch, Robin, Kuebler, Baker & *Turner* [22] have shown that the first band in the PE. spectrum of cyclopropane suffers a *Jahn-Teller* split of about 0.8 eV. This is in agreement with the prediction that this band corresponds to an ionization process in which the leaving electron vacates the $\mathbf{e}'$ orbital. The center of the band lies at $(10.5 + 11.3)/2 = 10.9$ eV, which, according to (1), yields $\varepsilon(\mathbf{e}') = -10.9$ eV. This result is in agreement with values reported by *Dewar* & *Worley* [14] (see also *Turner* [23]).

Comparing the observed *Jahn-Teller* splits in the PE. spectra of cyclopropane (0.8 eV), nor-tricyclene (**8**) (0.7 eV), hexahydrobullvalene (**4**) (0.6 eV), and bullvalene (**1**) (0.4 eV), we note that the size of the split decreases as the *e*-orbital spreads out over more and more centers. This is in agreement with expectation.

Substitution of the cyclopropane ring by sp^3-hybridized carbon atoms shifts the center of the split $\mathbf{e}'$-band towards lower ionisation potentials. For example, we find for nor-tricyclene (**8**) $\varepsilon(\mathbf{e}') = -9.7$ eV (*Jahn-Teller* split 0.7 eV) [18] and for hexahydrobullvalene (**4**) $\varepsilon(\mathbf{e}') = -9.3$ eV (*Jahn-Teller* split 0.6 eV). This means that the shift per sp^3-C-substituent amounts to approximately $\delta\varepsilon \sim 0.5$ eV, or a little less than the effect on a double bond π-orbital.

Preliminary results concerning the PE. spectra of vinyl-cyclopropane (**9**) and related compounds indicate that substitution of the cyclopropane ring by a vinyl group shifts the orbital energy $\varepsilon(\mathbf{e}')$ by about 0.2 eV towards higher energies [18]. In addition there is, of course, a strong conjugative interaction between the $\mathbf{e}_A$-orbital of the cyclopropane moiety in **9** and the π-orbital of the vinyl group, which yields a split of roughly 2.6 eV and thus a resonance integral β of ≈ 2.2 eV. This is of the same order as that between two conjugated π-bonds in a diene (from butadiene: $\beta = 2.38$ eV [18]). This result, while in agreement with conclusions reached from considerations of the stabilizing influence of cyclopropyl substituents in cyclopropyl-substituted carbonium ions [24], may seem nevertheless surprising. However, it is substantiated by the analysis of the PE. spectra of the compounds **1** to **3**.

σ-Orbitals. – Finally we shall make use of the observation [18] that the successive introduction of double bonds into a saturated hydrocarbon tends to shift the onset of the σ-bands in the PE. spectrum towards higher ionisation potentials. This shift is of the order of 0.5 to 0.6 eV per double bond for systems of the size of norbornane or bicyclo[2.2.2]octane, which contain 7 and 8 carbon atoms respectively. The reason for this shift is probably the increased 2*s*-character of the σ-frame.

We shall now show that this information is sufficient for a complete qualitative rationalisation of the PE. spectra of the hydrocarbons **1** to **5**.

Interpretation of the PE. spectra of the hydrocarbons 1 to 5. – In the following qualitative discussion we shall assume idealized structures for the molecules **1** to **5**. While the structure of **1** has been shown to be of C_{3v} symmetry by X-ray analysis [25], that of **4** is presumably only C_3 rather than C_{3v}. However, this ambiguity is irrelevant to our discussion. As far as **2**, **3** and **5** are concerned, their PE. spectra will be explained in terms of a structure of C_s symmetry, even though models suggest that **2** and **3** do not contain a mirror plane in their conformation of minimum energy.

With reference to fig. 3, the derivation of a correlation diagram for the sets of upper occupied molecular orbitals in the molecules **1** to **4** is based on the following assumptions:

Basis orbitals. – 1. In **4** the orbital energy $\varepsilon(\mathbf{e})$ of the *Walsh* orbitals **e** (corrected for *Jahn-Teller*-splitting) is taken to be $\varepsilon(\mathbf{e}) = -9.3$ eV. This is the experimental value found for the center of the first band in the PE. spectrum of **4**. (Here and in the following, the energies $\varepsilon(\mathbf{e})$ of the basis-*Walsh*-orbitals are indicated in fig. 3 by a triangular dot: ▲.)

2. According to the above discussion concerning the influence of substituents on the orbital energy of the *Walsh* orbitals, the value $\varepsilon(\mathbf{e})$ for **1** should be that of $\varepsilon(\mathbf{e}')$ observed in the PE. spectrum of cyclopropane, corrected for the destabilizing influence of the three double bonds, *i.e.* $\varepsilon(\mathbf{e}) = \varepsilon(\mathbf{e}') + 3 \cdot \delta\varepsilon = -10.8 + 3 \cdot 0.2 = -10.2$ eV.

3. Accordingly the energies $\varepsilon(\mathbf{e})$ of the basis-*Walsh*-orbitals **e** in **2** and **3** have been linearly interpolated between those of **1** and **4** as a function of N, the number of double bonds in the molecule (N = 0, 1, 2, 3):

$$\varepsilon_N(\mathbf{e}) = (-9.3 - 0.3\,N)\ \text{eV}\,. \qquad (3)$$

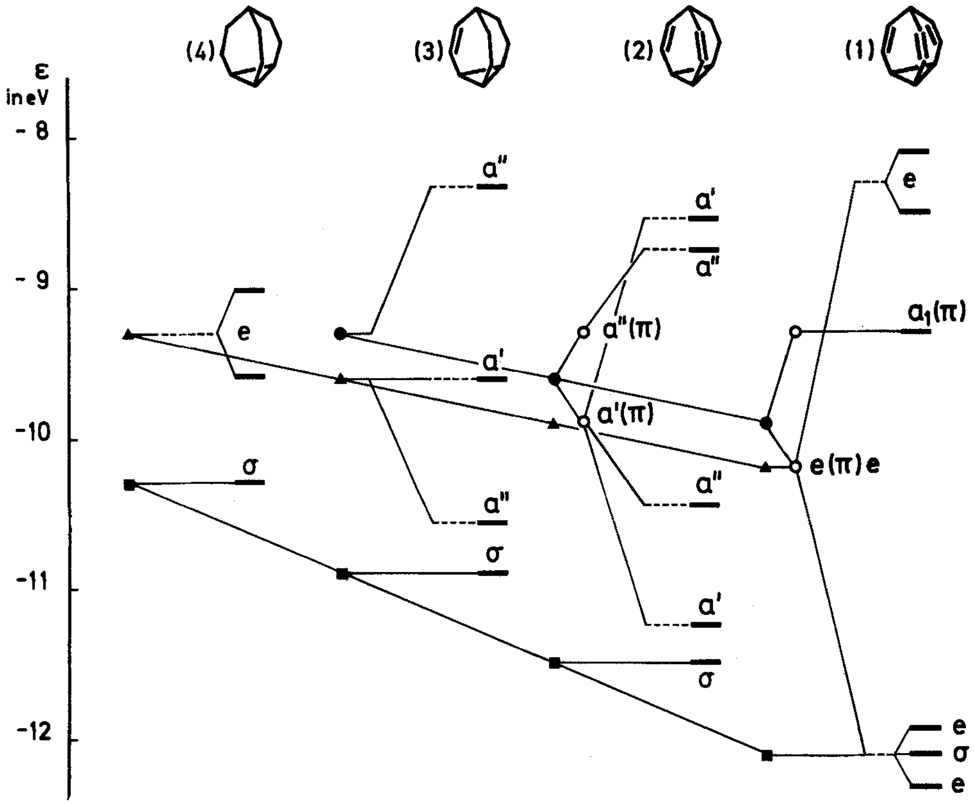


Fig. 3. *Orbital correlation diagram for the sets of upper occupied molecular orbitals in the molecules* **1** *to* **4**
For the significance of the symbols ▲, ●, ■ and ○ see text.

4. The energy $\varepsilon(\pi)$ of a non-interacting π-orbital in **3** is assumed to be $\varepsilon(\pi) = -9.3$ eV, that is, lower by -0.2 to -0.3 eV than for an isolated π-bond in bicyclo[2.2.2]octene or norbornene. This is equivalent to the assumption that the simultaneous presence of a cyclopropane ring in the molecule leads to a depression of the orbital energy $\varepsilon(\pi)$ in about the same fashion as the presence of a second double bond. (Here and in the following, the energies $\varepsilon(\pi)$ of the basis π-orbitals are indicated as in fig. 3 by round dots: ●.)

5. The dependence of $\varepsilon(\pi)$ on N, the number of double bonds in the molecule, manifests itself again in a depression of -0.3 eV for each additional double bond. This leads to the expression

$$\varepsilon_{N}(\pi) = \left(-9.3 - 0.3\,(N - 1)\right)\,\text{eV}\,, \tag{4}$$

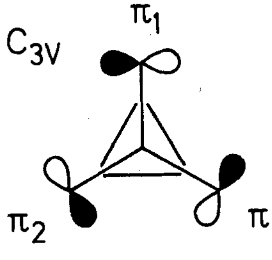
which is valid for N = 1, 2, 3.

6. The onset of the σ-bands in the PE. spectrum of **4** is located at -10.3 eV. From previous experience a shift of -0.5 to -0.6 eV is expected with the introduction of each additional double bond for a molecule of the size of **4**. This leads us to expect the following relationship for $\varepsilon_{\text{onset}}(\sigma)$:

$$\varepsilon_{N,\text{onset}}(\sigma) = (-10.3 - 0.6\,N)\,\text{eV}\,. \tag{5}$$

Here N can take the values 0, 1, 2, and 3. (The corresponding energies are plotted in fig. 3 as square dots: ■.)

Interaction terms. – 7. The phases of the π-orbitals in **1** and **2** are defined as follows:



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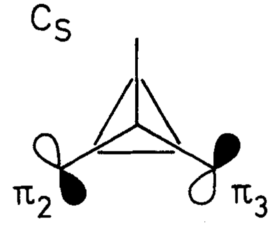


2

These π-orbitals interact with each other, mainly through-space, to about the same extent as in bicyclo[2.2.2]octadiene (**7**) [19]:

$$\varkappa_{ij} = \langle\pi_1\,|\,\mathcal{H}\,|\,\pi_2\rangle = \langle\pi_2\,|\,\mathcal{H}\,|\,\pi_3\rangle = \langle\pi_3\,|\,\mathcal{H}\,|\,\pi_1\rangle = 0.3\,\text{eV}\,. \tag{6}$$

Note that the phases of the π-orbitals have been defined in such a way that all overlap-integrals $\langle\pi_i|\pi_j\rangle = S$ are negative, so that the matrix elements $\varkappa_{ij} = \langle\pi_i|\,\mathcal{H}\,|\pi_j\rangle$ become positive quantities. Hence, the linear combinations associated with the bonding and antibonding levels (with respect to $\varepsilon(\pi)$) are in ZDO-approximation:

$$\begin{aligned}
&(1) \quad \mathbf{a}'_1(\pi) = \frac{1}{\sqrt{3}}\,(\boldsymbol{\pi}_1 + \boldsymbol{\pi}_2 + \boldsymbol{\pi}_3) \qquad \text{antibdg.}\\
&\left.\begin{aligned}
\mathbf{e}_S(\pi) &= \frac{1}{\sqrt{2}}\,(\boldsymbol{\pi}_2 - \boldsymbol{\pi}_3)\\
\mathbf{e}_A(\pi) &= \frac{1}{\sqrt{6}}\,(2\boldsymbol{\pi}_1 - \boldsymbol{\pi}_2 - \boldsymbol{\pi}_3)
\end{aligned}\right\} \text{bondg.}
\end{aligned} \tag{7}$$

$$\begin{aligned}
&(2) \quad \mathbf{a}''(\pi) = \frac{1}{\sqrt{2}}\,(\boldsymbol{\pi}_2 + \boldsymbol{\pi}_3) \quad \text{antibdg.}\\
&\qquad\ \ \mathbf{a}'(\pi) = \frac{1}{\sqrt{2}}\,(\boldsymbol{\pi}_2 - \boldsymbol{\pi}_3) \quad \text{bondg.}
\end{aligned} \tag{8}$$

The corresponding orbital energies are calculated with reference to (4) and (6) to be:

$$\begin{aligned}
(1) \quad & \varepsilon(\mathbf{a}'_1(\pi)) = \varepsilon_3(\boldsymbol{\pi}) + 2\,\varkappa_{ij} = -9.3\ \text{eV}\\
& \varepsilon(\mathbf{e}(\pi)) \ \ = \varepsilon_3(\boldsymbol{\pi}) - \varkappa_{ij} \ \ = -10.2\ \text{eV}\\
(2) \quad & \varepsilon(\mathbf{a}''(\pi)) = \varepsilon_2(\boldsymbol{\pi}) + \varkappa_{ij} \ \ = -9.3\ \text{eV}\\
& \varepsilon(\mathbf{a}'(\pi)) \ = \varepsilon_2(\boldsymbol{\pi}) - \varkappa_{ij} \ \ = -9.9\ \text{eV}
\end{aligned} \tag{9}$$

(These values are indicated in the diagram of fig. 3 as round, open dots: ○.)

8. Finally we have to assign a value to the resonance integral β between the $2\,\boldsymbol{p}_i$-orbitals that form the basis of the *Walsh* orbitals (2) and the $2p$-orbitals of $\boldsymbol{\pi}_i$ in α-position to the cyclopropane ring. It is found that the appropriate value of β is only slightly smaller than that quoted above (*i.e.* -2.2 eV), namely:

$$\beta = \langle 2\,\boldsymbol{p}_i\ (\textit{Walsh}) \mid \mathcal{H} \mid 2\,\boldsymbol{p}(\boldsymbol{\pi}_i)\rangle = \sqrt{2}\ \langle 2\,\boldsymbol{p}_i\ (\textit{Walsh}) \mid \mathcal{H} \mid \boldsymbol{\pi}_i\rangle = -1.9\ \text{eV}\,. \tag{10}$$

In the molecules **1** to **3**, the interaction defined by (10) will mix the symmetry-correct linear combinations of π-orbitals with those *Walsh* orbitals which belong to the same irreducible representation of the group. The relevant matrix elements are:

$$\begin{aligned}
(1) \quad & \langle \mathbf{e}_S(W) \mid \mathcal{H} \mid \mathbf{e}_S(\pi)\rangle = \beta = -1.9\ \text{eV}\\
& \langle \mathbf{e}_A(W) \mid \mathcal{H} \mid \mathbf{e}_A(\pi)\rangle = \beta = -1.9\ \text{eV}\\
(2) \quad & \langle \mathbf{e}_S(W) \mid \mathcal{H} \mid \mathbf{a}'(\pi)\rangle = \frac{1}{\sqrt{2}}\,\beta = -1.34\ \text{eV}\\
& \langle \mathbf{e}_A(W) \mid \mathcal{H} \mid \mathbf{a}''(\pi)\rangle = \frac{1}{\sqrt{6}}\,\beta = -0.78\ \text{eV}\\
(3) \quad & \langle \mathbf{e}_S(W) \mid \mathcal{H} \mid \boldsymbol{\pi}_1\rangle \ \ = \frac{1}{\sqrt{3}}\,\beta = -1.10\ \text{eV}
\end{aligned} \tag{11}$$

Solving the correspondent secular determinant results in the orbital energies given in the diagram of fig. 3 (dotted levels for the e-orbitals, solid lines for all others).

9. The e-levels give rise to a split band in the PE. spectrum because of a *Jahn-Teller* effect. The size of the split has been taken from the experimental values to be

0.4 eV in **1** and 0.6 eV in **4**. This leads to the final orbital scheme of fig. 3 shown in heavy solid lines.

The predictions derived from our model are compared with the experimental results in fig. 4. The agreement is as good as could reasonably be expected. It could be improved by optimizing the parameters (3), (4), (5), (6) and (10), *e.g.* by reducing β to -1.7 eV for **1**, but such a procedure would be totally unwarranted by our crudely simplified model.

To test the validity of our qualitative treatment, and thus of the correlation diagram of fig. 3, we have carried out a calculation for **1** and **2**, using the extended *Hückel* model (EHT) of *Hoffmann* [10]. It is our experience that this treatment yields in most cases the same relative ordering of the upper occupied orbitals of a molecule (*i.e.* sequence of irreducible representations) as does an SCF-calculation of the CNDO [26] or the MINDO [27] type, even though the absolute orbital energies may be seriously in error. As a further check, the assignment of orbitals proposed for **2** has been correlated on the basis of EHT calculations with that of homotropylidene (**5**), whose PE. spectrum is reproduced in fig. 2. The results of such a correlation, which are shown in fig. 5, provide convincing support for the assignment derived qualitatively in fig. 3.

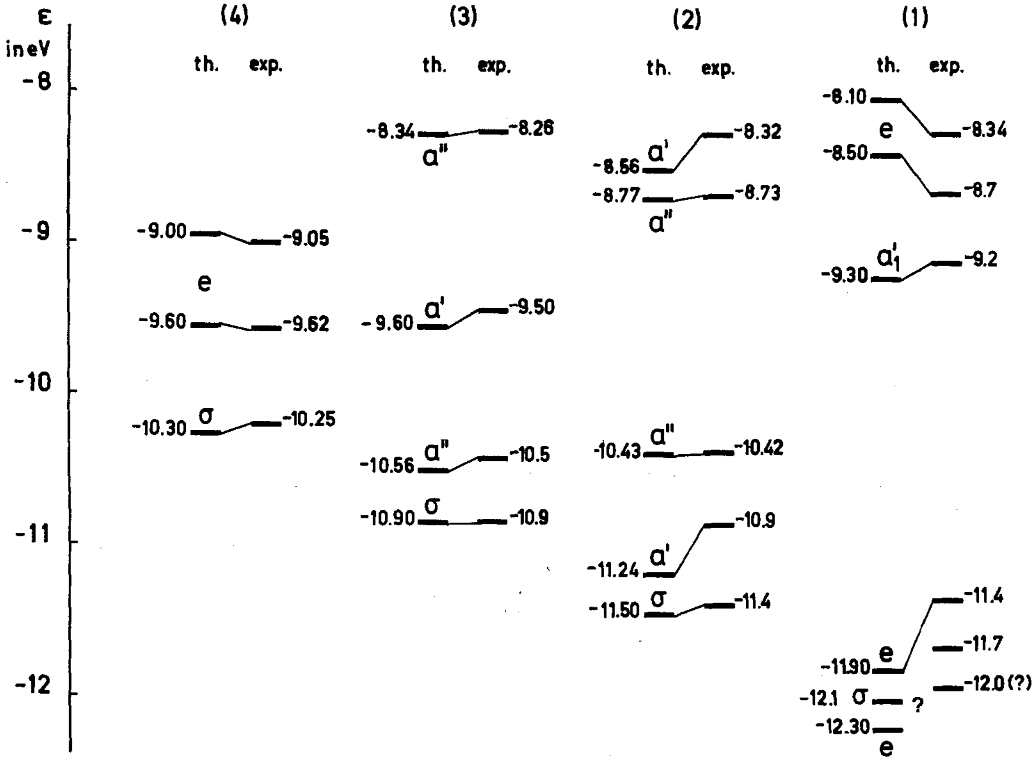


Fig. 4. *Comparison of the data derived in fig. 3 with the experimental values (table)*

The two levels in the column labelled CHD in fig. 5 are those calculated for the linear combinations $\mathbf{a}'(\pi)$ and $\mathbf{a}''(\pi)$ of the two π-orbitals of 1,4-cycloheptadiene, under the assumption that this molecule has C_s symmetry. The split $\varepsilon(\mathbf{a}''(\pi)) - \varepsilon(\mathbf{a}'(\pi)) = 0.45$ eV is due mainly to the through-space interaction of the π-bonds, which places $\mathbf{a}''(\pi)$ above $\mathbf{a}'(\pi)$. In **5** the relative conformation of the π-bonds with respect to the cyclopropane ring corresponds to the perpendicular conformation (b) rather than to the bisected one (a). For this reason we expect that there will be little mixing between the $\mathbf{a}'(\pi)$, $\mathbf{a}''(\pi)$-orbitals of the cycloheptadiene moiety of **5** with the *Walsh-e*-orbitals of the cyclopropane ring. This expectation is confirmed by the results of the EHT calculations summarized in column **5** of fig. 5. The split $\varepsilon(\mathbf{a}''(1)) - \varepsilon(\mathbf{a}'(1)) = 0.39$ eV is essentially the same as in 1,4-cycloheptadiene, the antisymmetric orbital $\mathbf{a}''(1)$ still lying above the symmetric one $\mathbf{a}'(1)$. The orbitals $\mathbf{a}''(2)$ and $\mathbf{a}'(2)$, which are in first approximation identical with $\mathbf{e}_A$ and $\mathbf{e}_S$ of the unperturbed cyclopropane ring, are split by only 0.18 eV. These computed values for the orbital splits have to be compared with the experimental values derived from the PE. spectrum of **5** (fig. 4): $\varepsilon(\mathbf{a}''(1)) - \varepsilon(\mathbf{a}'(1)) = 0.67$ eV and $\varepsilon(\mathbf{a}''(2)) - \varepsilon(\mathbf{a}'(2)) = 0.44$ eV.

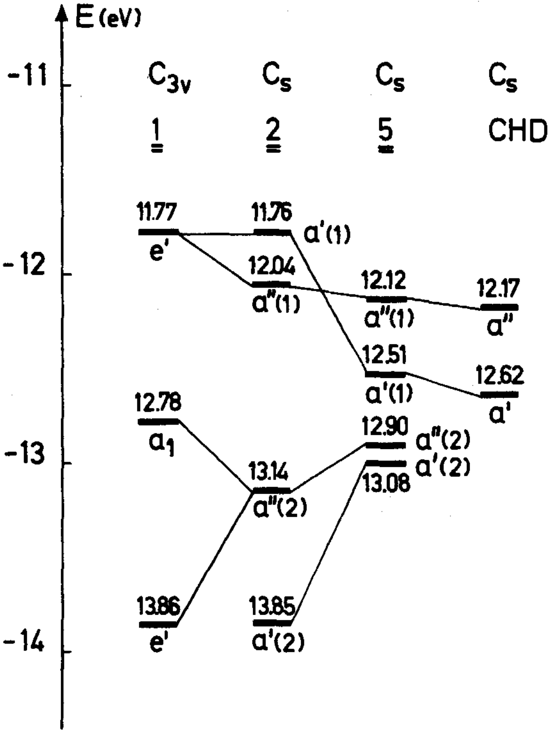


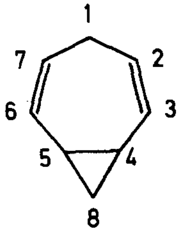
Fig. 5. *Orbital correlation diagram for bullvalene* (**1**), *dihydrobullvalene* (**2**), *homotropylidene* (**5**), *and 1,4-cycloheptadiene based on extended* Hückel *calculations*

The levels are classified with respect to the group C_s for dihydrobullvalene (**2**), homotropylidene (**5**) and 1,4-cycloheptadiene, and C_{3v} for bullvalene (**1**).

In the molecule **2** the conformation of the two double bonds with respect to the cyclopropane ring corresponds to the bisected conformation (a), and we expect therefore considerable interaction between the linear combinations $\mathbf{a}''(\pi)$, $\mathbf{a}'(\pi)$ of the π-orbitals and the components $\mathbf{e}_A$, $\mathbf{e}_S$ of the *Walsh-e*-orbitals respectively. As seen from the coefficients of the atomic orbitals $2\boldsymbol{p}_i$ in the linear combinations $\mathbf{e}_S$ and $\mathbf{e}_A$ given in the formulae (2), the interaction between $\mathbf{a}'(\pi)$ and $\mathbf{e}_S$ must be larger by a factor of $\sqrt{6}/\sqrt{2} = 1.73$ than the interaction between $\mathbf{a}''(\pi)$ and $\mathbf{e}_A$. Furthermore this direct conjugation will now dominate the through-space interaction, because of the large value of the resonance integral β between the $2\boldsymbol{p}_i$-basis orbitals of the double bonds. (The integral β has been defined in formula (10).) These expectations are again supported by the results of the EHT calculation shown in column **2** of fig. 5. The most noteworthy feature is the reversal of the sequence $\mathbf{a}'(1)$, $\mathbf{a}''(1)$ relative to that found in **5**. The spacings calculated are $\varepsilon(\mathbf{a}'(1)) - \varepsilon(\mathbf{a}''(1)) = 0.28$ eV, $\varepsilon(\mathbf{a}''(1)) - \varepsilon(\mathbf{a}''(2)) = 1.10$ eV, and $\varepsilon(\mathbf{a}''(2)) - \varepsilon(\mathbf{a}'(1)) = 0.71$ eV. These compare well with the respective experimental values of 0.41 eV, 1.10 eV, and 0.48 eV.

Finally, column **1** of fig. 5 gives the results of an EHT calculation for bullvalene (**1**), which completes the correlation diagram. (For obvious reasons the calculation does not include the prediction of the *Jahn-Teller* split of the *e*-orbitals, and the computed orbital energies refer therefore to the centers of the splitted bands). The step from **2** to **1** can be visualized by introducing into the orbital scheme of **2** a third π-orbital (π_1 in our nomenclature) which is antisymmetric with respect to the plane of symmetry of **2**. On the ε-scale, π_1 will occupy a level intermediate to those of $\mathbf{a}''(1)$ and $\mathbf{a}''(2)$, and its interaction with them will therefore lead to a destabilization of $\mathbf{a}''(1)$ and a stabilization of $\mathbf{a}''(2)$. For symmetry reasons (**1** belongs to the group C_{3v}) the magnitudes of these effects will be such that the mixed orbitals become part of $\mathbf{e}'(1)$ and $\mathbf{e}'(2)$ of **1** respectively. The third linear combination is the orbital $\mathbf{a}_1$. The calculated spacings are $\varepsilon(\mathbf{e}'(1)) - \varepsilon(\mathbf{a}_1) = 1.00$ eV and $\varepsilon(\mathbf{a}_1) - \varepsilon(\mathbf{e}'(2)) = 1.10$ eV, while the corresponding observed values are 0.64 eV and 2.40 eV.

Although the predicted orbital diagrams of **2** and **5** (fig. 5) are fundamentally different, both with respect to the sequence of the symmetry behaviour of the orbitals and to their spacing, the *Mulliken* overlap populations [28] of those bonds, which would be involved in a *Cope* rearrangement, are practically the same:



Mulliken overlap population

bond	Dihydro-bullvalene (**2**)	Homo-tropylidene (**5**)
2–7	– 0.04	– 0.05
2–3	1.29	1.30
3–4	0.88	0.84
4–5	0.61	0.66

Therefore these static indices do not permit any prediction about the ease with which this rearrangement can occur. It is known that **5** undergoes a *Cope* rearrangement only if it is in the *syn*-conformation, *i.e.* when the relative orientation of the double bonds and the cyclopropane ring corresponds to the bisected conformation (a) [9].

Experimental. – The PE. spectra have been recorded on a modified PS-15 Photoelectron Spectrometer (*Perkin-Elmer Ltd.*, Beaconsfield, England) of the type described by *Turner* [29]. (DC-powered, open He discharge yielding 21.21 eV photons (584 Å); electrostatic focussing sector of 5 cm radius and $\pi/\sqrt{2} = 127°$ deflection angle; optimum resolution 0.015 eV for electrons of 5.46 eV kinetic energy; resolution used in the present work ~0.02 eV). The ordinates in the spectra shown in fig. 1 and 2 are count-rates in arbitrary units. The general fall-off in intensity of the spectra with increasing ionisation potentials is an artefact due to the design of the spectrometer. The abscissa is calibrated relative to the ionisation potentials of an Ar/Xe mixture and to that of water (12.62 and 13.00 eV), which is often present in minute traces in samples of unsaturated hydrocarbons. Traces of water give rise also to the fine structure observable in the region from 14 to 16 eV (mean spacing 0.13 eV). In view of the small amount of sample, it was not possible to dry the compounds sufficiently without loss of material. Owing to the high vapour pressure and high ionisation cross-section, even traces of water produce sharp, characteristic water signals in the PE. spectrum.

Gas-chromatography revealed that the sample of **3** used in our investigation contained about 5 percent of **4** and the same amount of an unknown compound. As far as our conclusions are concerned, these impurities have no influence, as they do not interfere with the determination of the positions of the strong bands at lower ionisation potentials.

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195. Die Glykoside der Wurzeln von *Xysmalobium dilatatum* WEIMARCK. 1. Mitteilung: Isolierungen¹)

Glykoside und Aglykone, 327. Mitteilung

von **L. Meister, H. Kaufmann, W. Stöcklin** und **T. Reichstein**

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(5. VIII. 70)

Summary. The roots of *Xysmalobium dilatatum Weimarck* contain uzarin and xysmalorin as major glycosides. The same two compounds are also present as main components in the glycoside mixture from the roots of *Xysmalobium undulatum*. In addition to that, *X. dilatatum* also contains appreciable amounts of pregnane derivatives, linked to 2-deoxy-sugars. Four such xanthydrol-positive compounds (the dilatoides A, B, C and D) have been isolated in amorphous but pure or nearly pure form; they have not been detected in the roots of *X. undulatum*.

Xysmalobium dilatatum Weimarck [2] ist eine seltene Asclepiadacee, die bisher nur in Südrhodesien gefunden wurde. Sie steht dem weiter verbreiteten *Xysmalobium undulatum (L.) Ait. f.* sehr nahe und wird von *Bullock* [3] als Synonym zu diesem gezogen, ebenso das *X. amplifolium Weimarck*. Dagegen schreibt *Pole Evans* (in lit. 3. 6. 1958)³):

«I have at last got material of *Xysmalobium amplifolium Weimarck* and *X. dilatatum Weimarck* for you. Both plants are from the type localities. I have also Dr. *Weimarck*'s confirmation that my determinations of the herbarium material of both plants submittet to him are correct.

The roots of both plants are bitter and different in structure and taste.

In the field the plants are quite distinct from *X. undulatum* and can be picked out at once.

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¹) Auszug aus Dissertation *L. Meister*, Basel 1967.

²) 326. Mitt.: *Saner, Zerlentis, Stöcklin & Reichstein* [1].

³) Dr. *J. B. Pole Evans* war einer der besten Kenner der afrikanischen Flora; er ist leider am 16. Oktober 1968 im Alter von 89 Jahren gestorben.