

Les résultats précédents nous permettent de considérer que l'un des deux cycles triazoles exercerait peu de contrainte sur l'autre en maintenant la libre rotation autour de la liaison C(3)—N(4'). L'angle de rotation est fonction de deux énergies antagonistes. La première est l'énergie de résonnance correspondant à la délocalisation électronique entre les deux noyaux triazoliques. La deuxième est due aux forces de répulsion qui apparaissent entre les substituants quand ils existent liés aux atomes de carbone C(3) et C(5') et le doublet libre des atomes d'azote N(4) et N(2).

En ce qui concerne le bitriazole-3,4', molécule non substituée donc ne présentant pas de gêne stérique, l'écart faible à la coplanéité est dû probablement à une répulsion électronique entre les paires d'électrons libres des atomes d'azote N(4), N(2) et les hydrogènes H(3'), H(5'). Ce dernier point avait été soulevé par Murrel, Gil & Van Duijneveld (1965) au cours d'une discussion concernant le phényl-2 pyridine et le bipyridyl-2,2'. Dans ces molécules la coplanéité n'est empêchée que par les interactions stériques entre atomes CH...CH et CH...N. La Fig. 2 montre l'empilement moléculaire dans la maille. Les molécules presque planes sont disposées d'une manière alternée approximativement suivant la rangée [101]. La distance interplanaire est de l'ordre de 3,34 Å. Cette valeur est comparable à celle trouvée dans le graphite où la cohésion interplanaire est assurée par des liaisons de van der Waals. Ce qui explique le clivage très facile de ces cristaux.

L'angle dièdre obtenu par radiocristallographie est parfaitement cohérent avec le résultat qualitatif obtenu en spectroscopie ultraviolette du bitriazole-3,4' ( $\lambda_{\max} = 283$  nm, EtOH) (Aouial, 1989). En effet Domiano (1977) a étudié la structure du bitriazole-

4,4' et a trouvé  $91,9^\circ$  pour l'angle dièdre de la jonction N(4)—N(4'). Le spectre UV (EtOH) de cette dernière molécule présente une bande d'absorption vers 215 nm. Les résultats cristallographiques expliquent la valeur trouvée en UV pour le bitriazole-3,4'.

Nous adressons nos remerciements à M le Professeur H. Wondratscheck, directeur de l'Institut für Kristallographie der Universität Karlsruhe (TH), pour la collecte des données et la fructueuse discussion.

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## Structure of Diethyl 1,2,3,3b,4a,5,6,7,8,8a,8b,9-Dodecahydro-1,5-dioxo-4,8,9-metheno-4H-cyclopenta[1,2-a:4,3-a']dipentalene-4,10-dicarboxylate

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**Abstract.** C<sub>24</sub>H<sub>24</sub>O<sub>6</sub>,  $M_r = 408.45$ , triclinic,  $P\bar{1}$ ,  $a = 10.276$  (2),  $b = 13.000$  (2),  $c = 7.782$  (1) Å,  $\alpha =$

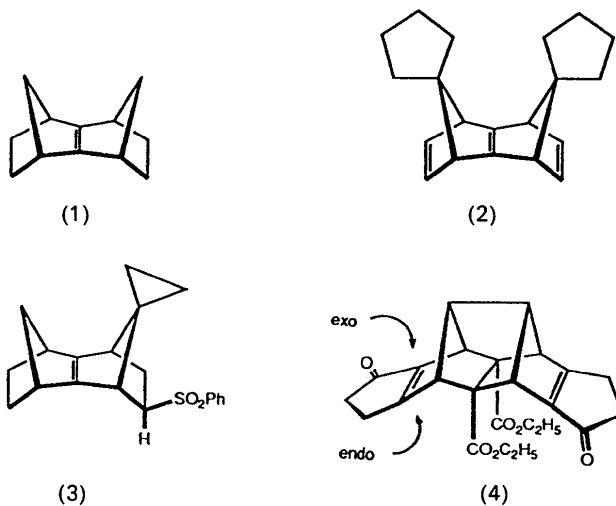
$98.06$  (1),  $\beta = 97.63$  (1),  $\gamma = 84.43$  (1) $^\circ$ ,  $V = 1017$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.33$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.89$  cm<sup>-1</sup>,  $F(000) = 432$ ,  $T = 296$  K,  $R = 0.048$  for 3321 unique reflections with  $F_o^2 > 3\sigma(F_o^2)$ . Both cyclopentenones are canted in the *endo* direction ( $6.0$  and  $7.9^\circ$ ), the one *syn* to the ethoxy groups less so for

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steric reasons. When the ester groups are disregarded, the polyquinane portion of the molecule is seen to possess a non-crystallographic twofold axis. The overall molecular geometry is reconcilable with the absence of any significant alteration in the density maximum of the C—C  $\pi$  bonds at this level of downward pyramidalization.

**Introduction.** A fundamental problem for the physical-organic chemist is understanding why norbornenes possess double bonds that are bent downward in their ground state (Houk, Rondan, Brown, Jorgensen, Madura & Spellmeyer, 1983). This pyramidal distortion, which can be as large as  $8^\circ$  towards the *endo* direction (Pinkerton, Schwarzenbach, Stibbard, Carrupt & Vogel, 1981; Paquette, Schaefer & Blount, 1983; MacKenzie, Miller, Muir & Manojlovic-Muir, 1983), clearly contributes heavily to the *exo* stereoselective course of addition reactions to such molecules. The strong bias for norbornyl cation capture from the same direction (Brown, 1977) may rest similarly on structural factors. In any event, the phenomenon gives every indication of being additive. Deformation levels of  $16$ – $18^\circ$  materialize when two norbornyl systems are fused together in a *syn* fashion across the site of unsaturation as in (1) (Watson, Galloy, Bartlett & Roof, 1981; Hagenbuch, Vogel, Pinkerton & Schwarzenbach, 1981; Paquette, Charumilind, Böhm, Gleiter, Bass & Clardy, 1983; Paquette, Hayes, Charumilind, Böhm, Gleiter & Blount, 1983). When pairs of *endo* protons are removed, with concurrent introduction of peripheral double bonds, the steric deterrent to more accentuated folding is removed and the extent of deformation increases still more. The present maximum is held by (2), whose central flap angle is only  $157.3$  (4) $^\circ$  (Paquette, Shen & Krause, 1989; Paquette & Shen, 1990).



Although these extreme levels of distortion are accompanied by notably enhanced chemical reactivity (Paquette, Carr, Böhm & Gleiter, 1980; Böhm, Carr, Gleiter & Paquette, 1980; Paquette, Fischer, Browne & Doecke, 1985; Paquette, Künzer, Green, De Lucchi, Licini, Pasquato & Valle, 1986), including in particular a sensitivity to oxygen (Paquette & Carr, 1980), very recent experimental determination by X-ray methods of the electron density distribution in the central olefinic double bond of *syn*-sesquinorbornene (3) has demonstrated the density maximum to be displaced from the internuclear line in the *exo* direction to the extent of only  $0.1$  Å (Irgartinger, Deuter, Charumilind & Paquette, 1989). This striking observation suggests that  $\pi$ -orbital distortion need not parallel structural deformation of the double-bond system in the absence of some external perturbation.

Despite the rapid advances in this field, we are aware of few structural studies in which a norbornene double bond has been conjugated with one (Ermer, Bell & Mason, 1989; Bernardinelli, Thomas & Perret, 1986; Declercq, Germain & Henke, 1973) or two (Subramanyam, Bartlett, Iglesias, Watson & Galloy, 1982; Watson & Kashyap, 1985; Battiste, Griggs, Sackett, Coxon & Steel, 1987; Muir & Sim, 1968) carbonyl acceptor groups. This fact has tempted us to carry out an X-ray crystallographic analysis of the  $C_2$ -symmetric diketo diester (4). This molecule is a relatively early intermediate in our improved synthesis of dodecahedrane (Paquette, Weber, Kobayashi & Miyahara, 1988; Paquette, Wyvratt, Schallner, Muthard, Begley, Blankenship & Balogh, 1979). It might reasonably be supposed that conjugative influences normally operative with an  $\alpha,\beta$ -unsaturated carbonyl system could serve to offset at least some of the  $\pi$  deformation usually encountered. On the other hand, since the  $\pi$ -electron densities on either face are hardly affected and  $\pi$ - $\pi$  orbital conjugation is known to be capable of effective operation at dihedral angles of  $30^\circ$  and beyond (Shea, 1980; Blank, Haenel, Krüger, Tsay & Wientges, 1988), the intrinsically bent character of norbornene double bonds need not be altered from the norm for this reason. Our involvement with (4) was designed to provide a first glimpse at the actual conformation of molecules of this class.

**Experimental.** Crystals of the title compound (4) grew as extremely large, clear and colorless chunks. One of these crystals was cut several times in order to obtain a suitably sized fragment that measured approximately  $0.35 \times 0.38 \times 0.38$  mm. Examination of the diffraction pattern on a Rigaku AFC5S diffractometer with graphite-monochromated Mo  $K\alpha$  radiation indicated a triclinic crystal system with space group possibilities of  $P1$  or  $P\bar{1}$ . The

Table 1. Final positional coordinates and equivalent isotropic thermal parameters for (4)

The form of the equivalent isotropic thermal parameter is:  $B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ .

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
O(1)	0.7435 (2)	0.3523 (1)	0.5055 (2)	4.12 (7)
O(2)	1.4051 (2)	0.1252 (1)	1.3235 (3)	5.47 (8)
O(3)	1.1172 (1)	0.0310 (1)	0.7860 (2)	3.80 (6)
O(4)	1.2632 (1)	0.1500 (1)	0.8798 (2)	3.59 (6)
O(5)	1.0855 (2)	0.2867 (1)	0.6484 (2)	4.59 (8)
O(6)	1.1731 (1)	0.4131 (1)	0.8405 (2)	3.48 (6)
C(1)	1.0354 (2)	0.3060 (1)	0.9417 (2)	2.11 (6)
C(2)	0.8804 (2)	0.3261 (1)	0.9157 (2)	2.45 (7)
C(3)	0.8213 (2)	0.2617 (1)	0.7548 (2)	2.55 (7)
C(4)	0.7682 (2)	0.2728 (1)	0.5743 (3)	2.86 (8)
C(5)	0.7481 (2)	0.1623 (2)	0.4844 (3)	3.5 (1)
C(6)	0.8039 (2)	0.0880 (2)	0.6180 (3)	3.07 (8)
C(7)	0.8398 (2)	0.1616 (1)	0.7788 (2)	2.57 (7)
C(8)	0.9090 (2)	0.1554 (1)	0.9588 (2)	2.57 (7)
C(9)	1.0539 (2)	0.1851 (1)	0.9723 (2)	2.22 (7)
C(10)	1.0902 (2)	0.1934 (1)	1.1772 (2)	2.66 (7)
C(11)	1.2176 (2)	0.2413 (1)	1.2358 (2)	2.79 (7)
C(12)	1.3548 (2)	0.2106 (2)	1.2932 (3)	3.59 (9)
C(13)	1.4273 (2)	0.3093 (2)	1.3075 (4)	4.4 (1)
C(14)	1.3265 (2)	0.3953 (2)	1.2449 (3)	3.42 (9)
C(15)	1.2025 (2)	0.3409 (1)	1.2085 (2)	2.68 (7)
C(16)	1.0635 (2)	0.3641 (1)	1.1314 (2)	2.47 (7)
C(17)	0.9853 (2)	0.2866 (1)	1.2075 (2)	2.71 (7)
C(18)	0.8658 (2)	0.2617 (1)	1.0651 (2)	2.72 (7)
C(19)	1.1453 (2)	0.1134 (1)	0.8667 (2)	2.57 (7)
C(20)	1.3620 (3)	0.0869 (2)	0.7842 (5)	5.3 (1)
C(21)	1.4863 (4)	0.1378 (4)	0.830 (1)	9.5 (3)
C(22)	1.1004 (2)	0.3323 (1)	0.7938 (2)	2.38 (7)
C(23)	1.2374 (3)	0.4465 (3)	0.7031 (3)	4.9 (1)
C(24)	1.3703 (3)	0.4751 (3)	0.7753 (4)	6.3 (2)

unit-cell constants were determined at room temperature by the least-squares fit of the diffractometer setting angles for 25 reflections in the  $2\theta$  range 24 to  $30^\circ$ .

Intensities were measured by the  $\omega$ - $2\theta$  scan method for the  $2\theta$  range 4 to  $55^\circ$  ( $h \leq 13$ ,  $-16 \leq k \leq 16$ ,  $-10 \leq l \leq 9$ ). The scan speed used for data collection was  $4^\circ \text{ min}^{-1}$  in  $\omega$  with a maximum of four scans per reflection allowed. The scan range was  $(1.10 + 0.35 \tan \theta)^\circ$  in  $\omega$ . The crystal was stable during data collection as the intensities of six standard reflections (12 $\bar{1}$ , 101, 200, 6 $\bar{1}\bar{1}$ , 361 and 554), which were measured after every 150 reflections, did not vary significantly. The total number of reflections measured was 4935. Symmetry equivalents were averaged to give an  $R_{\text{int}}$  value of 0.013 (based on  $F^2$ ) and 4673 unique reflections. Data reduction, which included Lorentz and polarization corrections, and all further calculations were performed with the *TEXSAN* package of crystallographic programs (Molecular Structure Corporation, 1987).

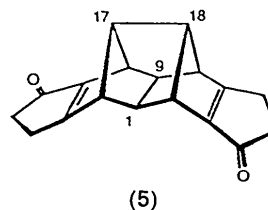
The structure was solved in  $P\bar{1}$  by the direct-methods program *MITHRIL* (Gilmore, 1983), and most of the non-H atoms were located on an electron density map. The remaining atoms were found by standard Fourier methods. All of the H atoms were ultimately located on difference electron density maps after the anisotropic stage of refinement. The H atoms were refined isotropically, with the exception of the three H atoms bonded to C(24). These three atoms were included in the model as fixed

contributions in their calculated positions based on idealized  $sp^3$  geometry and a C—H bond length of 0.98 Å. All of the least-squares refinements were full matrix and based on  $F$  so that the function minimized in least squares was  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/\sigma^2(|F_o|)$ .

The final refinement cycle was based on the 3321 intensities with  $F_o^2 > 3\sigma(F_o^2)$  and 355 variables and resulted in agreement indices of  $R = 0.048$ ,  $wR = 0.056$  and  $S$  (error in observation of unit weight) = 2.08 e.

For this final cycle  $(\Delta/\sigma)_{\text{max}}$  is 0.08 and the difference electron density map contains maximum and minimum peak heights of 0.30 and  $-0.34 \text{ e \AA}^{-3}$ . Scattering factors were obtained from the usual sources [C- and O-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71, 148) and H-atom scattering factors from Stewart, Davidson & Simpson (1965)]. Final positional parameters and equivalent isotropic thermal parameters are listed in Table 1.\*

**Discussion.** An *ORTEP* drawing of the molecule (Johnson, 1965) giving the numbering scheme is shown in Fig. 1. A stereoscopic view of the unit cell is displayed in Fig. 2.



Disregarding the diethyl ester groups, the polyquinane portion of the molecule defined by (5) contains a non-crystallographic twofold axis that passes through the C(1)—C(9) and C(17)—C(18) bonds. Selected bond lengths and angles for this fragment are listed in Table 2. Since the carbonyl portions of the diethyl ester groups are oriented basically in the same direction, the twofold symmetry is broken by the orientation of these groups. The C(1)—C(9) bond length of 1.612 (2) Å is seen to be slightly long for a C—C single bond. However, this is a reasonable value for a bond between two tetracoordinate C atoms (Osawa, Onuki & Mislow, 1981).

\* Tables of metrical parameters for the non-H atoms, least-squares planes, anisotropic thermal parameters, positional parameters and metrical parameters for the H atoms, and observed and calculated structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53920 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The deformation about the C(3)—C(7) and C(11)—C(15) double bonds is modest but significant. The dihedral angle,  $\psi$ , between the least-squares planes defined by C(10)—C(11)—C(15)—C(16) and C(11)—C(12)—C(14)—C(15) is  $6.0(2)^\circ$ , while the analogous angle for C(2)—C(3)—C(7)—C(8) and C(3)—C(4)—C(6)—C(7) is  $7.9(2)^\circ$ . Both five-membered rings are bent downwards, *i.e.* toward the ester groups, and each of these rings is slightly non-planar.

In view of the geometry characteristics of (4), it is clear that the ability of the cyclopentenone rings to fold in a downward direction is of the usual magnitude. Since this pyramidalization is sterically impeded to some extent by the underlying ethoxy-carbonyl groups, the smaller  $\psi$  of  $6.0^\circ$  in the case of that five-membered ring *syn* to the pair of  $-\text{OCH}_2\text{CH}_3$  groups is reasonable. We presume on this basis that the  $\psi$  of  $7.9^\circ$  is more closely representative of the level of deformation that these systems would prefer to adopt.

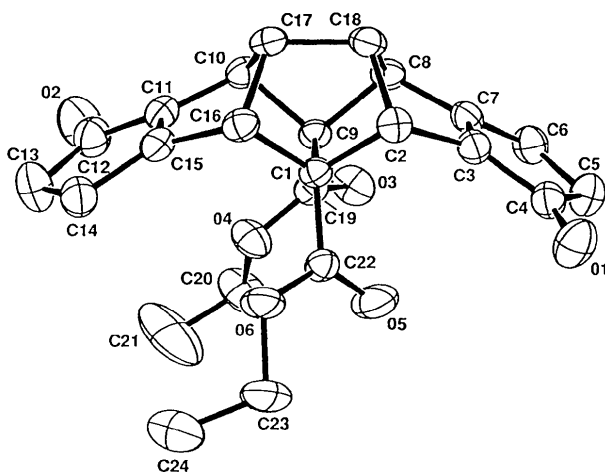


Fig. 1. An ORTEP (Johnson, 1965) drawing showing the atom-numbering scheme for (4). The hydrogen atoms are omitted for clarity; the non-hydrogen atoms are represented by 50% probability thermal ellipsoids.

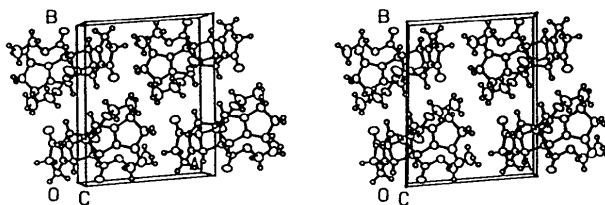


Fig. 2. Stereoscopic view of the unit cell.

Table 2. Selected metrical parameters for (4)

Bond lengths (Å)			
C(1)—C(16)	1.566 (2)	C(9)—C(8)	1.561 (3)
C(1)—C(2)	1.580 (3)	C(9)—C(10)	1.580 (3)
C(15)—C(16)	1.493 (3)	C(7)—C(8)	1.494 (3)
C(11)—C(15)	1.333 (3)	C(3)—C(7)	1.332 (3)
C(11)—C(11)	1.493 (3)	C(2)—C(3)	1.497 (3)
C(10)—C(17)	1.556 (3)	C(2)—C(18)	1.556 (3)
C(16)—C(17)	1.570 (3)	C(8)—C(18)	1.565 (3)
C(1)—C(9)	1.612 (2)	C(17)—C(18)	1.567 (3)
Bond angles (°)			
C(2)—C(1)—C(16)	98.9 (1)	C(8)—C(9)—C(10)	99.0 (1)
C(2)—C(1)—C(9)	101.6 (1)	C(10)—C(9)—C(1)	101.8 (1)
C(16)—C(1)—C(9)	102.8 (1)	C(8)—C(9)—C(1)	102.8 (1)
C(1)—C(16)—C(15)	111.7 (1)	C(9)—C(8)—C(7)	110.8 (1)
C(1)—C(16)—C(17)	91.7 (1)	C(9)—C(8)—C(18)	91.9 (1)
C(15)—C(16)—C(17)	103.4 (1)	C(7)—C(8)—C(18)	104.2 (1)
C(11)—C(15)—C(11)	108.2 (2)	C(8)—C(7)—C(3)	108.0 (2)
C(15)—C(11)—C(10)	108.9 (2)	C(7)—C(3)—C(2)	108.8 (2)
C(11)—C(10)—C(9)	111.7 (2)	C(3)—C(2)—C(1)	111.2 (1)
C(11)—C(10)—C(17)	103.3 (2)	C(3)—C(2)—C(18)	103.5 (1)
C(9)—C(10)—C(17)	91.8 (1)	C(1)—C(2)—C(18)	92.0 (1)
C(10)—C(17)—C(16)	93.8 (1)	C(8)—C(18)—C(2)	93.7 (1)
C(10)—C(17)—C(18)	105.2 (2)	C(2)—C(18)—C(17)	105.2 (1)
C(16)—C(17)—C(18)	105.4 (1)	C(8)—C(18)—C(17)	105.4 (1)

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## Sesquiterpene Lactones of the *Umbelliferae*. Structural Characterization of Badkhysin\* and its C(5)-Epimer, Isobadkhysin†

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**Abstract.** Badkhysin (III), C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>, *M<sub>r</sub>* = 344.407, monoclinic, *P*2<sub>1</sub>, *a* = 12.331 (2), *b* = 6.024 (1), *c* = 24.915 (5) Å, β = 98.03 (1)°, *V* = 1832.6 (6) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.25, *D<sub>m</sub>* = 1.25 Mg m<sup>-3</sup>, λ(Cu Kα) = 1.54178 Å, μ = 0.69 mm<sup>-1</sup>, *F*(000) = 736, *T* = 293 K, *R* = 0.063 for 3402 observed [*I* > 1.96σ(*I*)] reflections and 480 refined parameters. Isobadkhysin (IV), C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>, *M<sub>r</sub>* = 344.407, monoclinic, *P*2<sub>1</sub>, *a* = 13.082 (4), *b* = 5.184 (3), *c* = 14.212 (4) Å, β = 109.92 (2)°, *V* = 906.2 (7) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.26, *D<sub>m</sub>* = 1.24 Mg m<sup>-3</sup>, λ(Cu Kα) = 1.54178 Å, μ = 0.70 mm<sup>-1</sup>, *F*(000) = 368, *T* = 293 K, *R* = 0.046 for 1323 unique observed reflections [*I* > 1.96σ(*I*)] and 240 refined parameters. Initial assignment of the stereostructure of (III) is now revised on grounds of the X-ray analysis. (III) belongs to the 2-oxo-5β*H*,6α*H*,7α*H*-guaia-1(10),3-dien-6,12-olides which are characteristic for plants of the *Umbelliferae* family. Isomerization of (III), induced by alkali

treatment, takes place at C(5) as shown by the X-ray analysis of (IV).

**Introduction.** While naturally occurring sesquiterpene lactones are characteristic components in the species of the *Compositae* (daisy family) they are also present in other plant families of which the *Umbelliferae* (parsley family) takes the second place in a number of isolated and described sesquiterpene lactones. In the group of 2-oxoguaia-1(10),3-dien-6,12-olides two basic stereostructural types (I) and (II) can be distinguished which differ mainly in the configurations at C(5) and C(6). Our recent investigations indicate that the different stereostructural types are indicative of their differing plant sources (Holub & Buděšínský, 1986; Rychlewska, 1986). Guaianolides of type (I) with the 'usual' arrangement of substituents are synthesized in plants of the *Compositae*, while quaianolides of type (II) seem characteristic for the species of the *Umbelliferae*. Badkhysin (III), isolated from roots of *Ferula oopoda* (Boiss. et Buhse) Boiss. was initially assigned as belonging to the class of lactones with the basic stereostructure (I) (Serkerov, 1980) and was sub-

\* 8α-Angeloyloxy-2-oxo-5β*H*,6α*H*,7α*H*,11α*H*-guaia-1(10),3-dien-6,12-olide.

† 8α-Angeloyloxy-2-oxo-5α*H*,6α*H*,7α*H*,11α*H*-guaia-1(10),3-dien-6,12-olide.