Bisamides, Lignans, Triterpenes, and Insecticidal Cyclopenta[*b*]benzofurans from *Aglaia* Species[1]

G. Brader,[†] S. Vajrodaya,[†,‡] H. Greger,*[,†] M. Bacher,[§] H. Kalchhauser,[§] and O. Hofer[§]

Comparative Phytochemistry Department, Institute of Botany, University of Vienna, Rennweg 14, A-1030 Wien, Austria, Institute of Organic Chemistry, University of Vienna, Währingerstrasse 38, A-1090 Wien, Austria

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Twelve new derivatives of bisamides [piriferinol (**5**), edulimide (**7**)], lignans [lariciresinol acetat (**10**)], triterpenes [4-bis-norcycloartane-type triterpenes (**11a**, **12a**+**b**, **13a**+**b**)], cyclopenta[*b*]benzofurans [pannellin (**15**), pannellin 1-*O*-acetate (**16**), 3′-methoxypannellin (**17**)], and an aromatic butyrolactone [aglalactone (**18**)] were isolated and identified from lipophilic leaf, stem, and root extracts of *Aglaia* spp. *elaeagnoidea*, *edulis*, *grandis*, *silvestris*, and *tomentosa*. Two cyclopenta[*b*]benzofurans (flavaglines), pannellin (**15**) and pannellin 1-*O*-acetate (**16**), displayed very strong insecticidal activity against *Spodoptera littoralis* and *Lymantria dispar*, comparable with the activity of azadirachtin.

In connection with our current screening for biologically active compounds from Asian Rutaceae, samples from other families, especially from the order Rutales, were also routinely collected on field trips and tested for antifungal and insect toxicity properties. Compared with our best data from the genus *Glycosmis* (Rutaceae),[2,3] the lipophilic crude extracts of some *Aglaia* species of the family Meliaceae showed even better activity against the test insect, the cotton leaf worm *Spodoptera littoralis* (Lepidoptera, Noctuidae), and also against the gypsy moth *Lymantria dispar* (Lepidoptera, Lymantriidae). In survival and growth inhibition tests on the leaves, stem, and root bark, the root extracts of some collections were shown to possess the highest insecticidal activities. More detailed inspection of the corresponding voucher specimens[4] revealed that this high activity was attributed to different collections of *A. elaeagnoidea* (A. Juss.) Benth. [syn. *A. roxburghiana* (Wight & Arn.) Miq.]. The samples of *A. tomentosa* Teijsm. & Binn. and *A. grandis* Korth. ex Miq., displayed weaker activity, whereas in *A. silvestris* (M. Roemer) Merrill (syn. *pyramidata* Hance) and *A. edulis* (Roxb.) Wall. no insect toxicity could be detected at all. With respect to the many reports already existing on the insecticidal cyclopenta[*b*]-benzofuran (flavagline) derivatives of some *Aglaia* species,[5−7] we also expected corresponding derivatives in our samples as active principles.

Results and Discussion

Bioassay-guided fractionation of the root extract of *A. elaeagnoidea* with freshly hatched larvae of *S. littoralis* have shown that the most active compound was identical with the major component of the corresponding HPLC profile, representing a good source for isolation. Based on its characteristic UV spectrum and retention time, this compound could be detected in the HPLC profiles of all highly active samples of *A. elaeagnoidea* and was shown to accumulate in extracts of the root and stem bark, where it was accompanied by small amounts of related derivatives. All these compounds were identified as a new group of cyclopenta[*b*]benzofurans. The leaves, by contrast, were mainly characterized by a series of peaks with simple UV spectra, identified as bisamides and an as yet unknown lignan. Furthermore, they were shown to accumulate large amounts of triterpenoids, which were detected by TLC only, using anisaldehyde-sulfuric acid-methanol as a chromogenic spray.[49] Due to scarcity of plant material, the active compounds of *A. tomentosa* and *A. grandis* could not be determined by bioassay-driven fractionation. Based on HPLC−UV screening, both species, as well as the collections of *A. edulis* and *A. silvestris* were mainly characterized by an accumulation of bisamides and/or lignans. Derivatives from both classes of compound have already been reported for other *Aglaia* species,[8−15] and bisamides were shown to exhibit cytotoxic[12,14] and antiviral activity.[13]

Altogether the leaf extracts of the five *Aglaia* species investigated were shown to produce seven different bisamides containing either putrescine or the corresponding pyrrolidine ring as a diamine part always linked to two different acid moieties. In accordance with a previous report,[8] the putrescine diamide pyramidatine (**6**) was isolated as major component from *A. silvestris* (= *A. pyramidata*), but was now found also in small amounts in *A. grandis*. The pyrrolidine derivatives odorine (**1**) and odorinol (**2**), already described from *A. odorata* Lour.[9] and an Indian provenance of *A. elaeagnoidea*,[10] were now also isolated from a Thai collection of *A. elaeagnoidea*, and the related dehydroodorine (**3**)[12] was found as a minor constituent in the leaf extract of *A. tomentosa* collected in Malaysia. From this group, odorine (**1**) especially appears to be more widely distributed within *Aglaia* and has already been reported from *A. argentea* Blume and *A. forbesii* King[34] as well as from *A. elliptica* Blume (syn. *A. harmsiana* Perkins).[25] Besides the odorines (**1**, **2**), *A. elaeagnoidea* also accumulates piriferine (**4**), previously described from *A. edulis* (syn. *A. pirifera* Hance),[11] together with an unknown derivative (**5**). Apart from the different retention time, the IR and UV data of **5** were nearly identical with those of odorinol (**2**). Compared to the ^{1}H NMR spectrum of piriferine (**4**), the new compound **5** showed very similar data as far as the cinnamic acid and the pyrrolidine proton resonances are concerned.[8] In the second acid moiety the characteristic heptet for H-2 was

* To whom correspondence should be addressed. Tel: 43 1 4277 54070. Fax: 43 1 4277 9541. E-mail: greger@s1.botanik.univie.ac.at.
‡ Permanent address: Department of Botany, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand.
† Comparative Phytochemistry Department, Institute of Botany.
§ Institute of Organic Chemistry.

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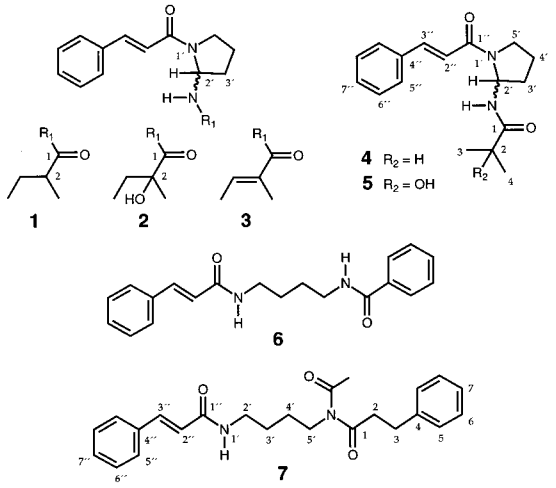
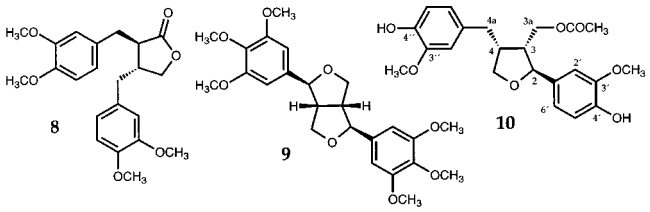
missing, and the two methyl doublets for Me-3 and Me-4 (δ 1.10 and 1.16 for **4**) changed to two downfield-shifted singlets at δ 1.35 and 1.46. The FDMS showed the molecular ion at *m/z* 302 and confirmed the proposed elemental formula ($C_{17}H_{22}N_2O_3$). By analogy to odorine/odorinol (**1**/**2**), compound **5** was designated as piriferinol. The specific rotation of piriferinol (**5**) is $[\alpha]^{20}_D$ +8°, but nothing can be said about its enantiomeric purity. At least partial racemizations at C-2′ may easily occur via a ring opening mechanism of the 2-amino-substituted pyrrolidine ring (acetal-like N−C−N arrangement). This behavior has already been described for compound **1**.[10] In that case, the equilibration at C-2′ is an epimerization due to a second center of chirality in the molecule. We suppose that different isolation procedures and crystallization techniques may have led to the isolation of different epimeric compositions of compounds **1** and **2**.[8−10,14] In our case, epimeric mixtures of **1** and **2** were clearly obtained, because in both compounds many lines in the NMR spectra were duplicated: C-1−C-5, C-3′−C-5′, and C-1″, C-3″ in the ^{13}C NMR spectrum with $\Delta\delta$ up to 0.2 ppm (average 0.1 ppm) and the sharp olefinic doublets for the cinnamic moiety (H-2″ and H-3″, $\Delta\delta$ 0.02−0.03 ppm) in the ^{1}H NMR spectrum. The ratio of epimers is about 1:1 (51:49) for **1** and 63:37 for **2**. Epimerization in $CDCl_3$, and therefore two sets of resonances for the two possible epimers, has been mentioned by Purushothaman et al.[10]



The HPLC profile of the leaf extract of *A. edulis* was characterized by a predominant compound that was shown to be a new bisamide derived from putrescine (**7**). In contrast to the already known pyramidatine (**6**) with cinnamic and benzoic acid moieties,[8] the new compound **7**, named edulimide, is the corresponding cinnamic/dihydrocinnamic acid bisamide with an additional acetic acid moiety forming an imide group. The ^{1}H and ^{13}C NMR spectra were rather conclusive and unambiguous concerning the above-mentioned structural components; however, the decision as to whether the acetyl group is at the nitrogen of the cinnamoyl or at the dihydrocinnamoyl amide moiety was still open. Attempts to clarify this via NOE measurements failed, because there were no enhancements between the acetyl−Me group and protons of one of the two acids. However, literature data for related imides of either cinnamic or dihydrocinnamic amides are strongly in favor of a dihydrocinnamic−acetic imide.[16−18] In the dihydrocinnamic amides the resonances for H_2-2 and H_2-3 are found at ca. 2.50 and 3.00 ppm, in imides both resonances shift to higher values of 2.80−3.30 ppm. Because no resonances were found in the region 2.50−3.10 ppm for compound **7**, a simple dihydrocinnamic acid amide could be excluded. However, the data obtained with chemical shifts between 3.30 and 3.60 ppm (unresolvable multiplets for H_2-2, H_2-3, H_2-2′, and H_2-5′) were compatible with a dihydrocinnamic acid imide. On the other hand, the resonances of the cinnamic acid moiety of **7** are the usual ones for simple amides. The proposed structure of edulimide (**7**) is therefore a cinnamic amide dihydrocinnamic−acetic imide of putrescine.

From the leaf extracts of *A. elaeagnoidea*, *A. tomentosa*, and *A. grandis* three different lignans were isolated and identified, which may be classified into three groups: *A. tomentosa* was characterized by the predominant (+)-methylarctigenin (**8**), a dibenzylbutyrolactone-type lignan, and *A. grandis*, by large amounts of (+)-yangambin (**9**), a sesamin(tetrahydrofurofuran)-type lignan. The structure of **8** was derived by comparison of our spectral data with a recent detailed NMR analysis[19] of (−)-methylarctigenin ($[\alpha]^{20}_D$ −32.2°). Concerning the absolute configuration, it is interesting to note that the (−)-enantiomer is described for many different natural sources but (+)-methylarctigenin seems to be rather scarce. The identical relative configuration for our compound **8**, together with the measured $[\alpha]^{20}_D$ +32°, was conclusive proof that the optical antipode of the usual (−)-enantiomer was isolated. (+)-Methylarctigenin, with $[\alpha]^{20}_D$ +32.2°, was obtained synthetically after racemate resolution.[20]



From *A. elaeagnoidea*, collected in southeast Thailand, we isolated a new derivative (**10**) of the substituted furan-type lignans as a major component. Because of its characteristic UV spectrum with two maxima at 230 and 282 nm (MeOH), **10** could easily be detected in the HPLC profiles of 10 individual samples from four different provenances. A related derivative, together with a diarylbutane lignan, has already been described from the bark of *A. elaeagnoidea* collected in Java.[15] Based on the IR data, the new lignan (**10**) possesses an ester function, indicated by strong signals at 1744 and 1236 cm^{-1}, and phenolic OH groups, indicated by a characteristic band at 3556 cm^{-1} (CCl_4). The molecular formula of $C_{22}H_{26}O_7$ was derived by HRMS. The ^{1}H and ^{13}C NMR spectra revealed the presence of three diastereotopic methylene groups, three CH (one doublet and two multiplets), two aromatic moieties with ABC spin systems for 1,3,4-trisubstituted benzene rings, two aromatic OCH_3 groups, and two phenolic OH groups, as well as an acetyloxy moiety. All these NMR data are compatible with a 3-acetyloxymethyl-4-benzyl-2-phenyl-tetrahydrofuran structure of compound **10**. This lignan type was derived unambiguously from the fragmentation pattern of the EIMS and from 2D NMR experiments. Prominent peaks at *m/z* 137 for the 4-hydroxy-3-methoxybenzyl ion (100%) and *m/z* 151 for the 4-hydroxy-3-methoxybenzaldehyd ion (87%), were in favor of a benzyl moiety and a 2-phenylfuran partial structure.[21] A strong C/H long-range cross peak from the carbonyl carbon atom to H_2-3a allowed the identification of the

Table 1. ^{1}H and ^{13}C NMR Data for Triterpenes **11a,b**−**14a,b** (250 MHz, $CDCl_3$, δ/ppm, TMS)[a]

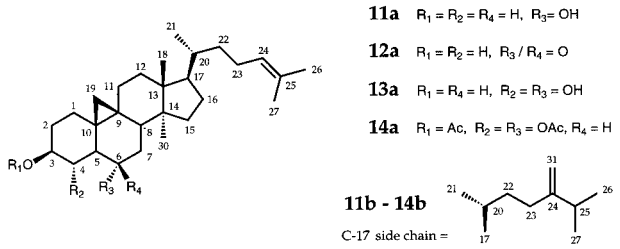
	^{1}H[b]				^{13}C[c]			
position	**11a**	**12a**	**13a**[d]	**14a**[c]	**11a**	**12a**	**13a**	**14a**[f]
1	1.58/1.24	1.67/1.47		1.64/1.28	30.9 t	29.1 t	30.4 t	29.7 t
2	1.99/1.37	2.03/1.33		2.07/1.57	34.7 t	33.8 t	31.6 t	29.0 t
3	3.70 dddd	3.67 dddd	3.51	4.90 ddd	71.1 d	70.8 d	76.1 d	74.9 d
4	2.41 br d[g]/1.13	2.46 br d[g]/1.18	3.55	5.07 dd	37.4 t	35.6 t	80.7 d	76.7 d
5	1.40	2.37 br d	1.50	2.05 dd	45.4 d	48.7 d	48.9 d	45.7 d
6	3.10 ddd		3.50	4.60 ddd	71.4 d	212.2 s	72.1 d	72.4 d
7	1.52/1.22	2.29/2.18		1.56/1.22	35.5 t	38.0 t	35.3*t	31.7 t
8	1.86	2.66 dd	1.80	1.88 m	47.1 d	40.1 d	46.8 d	45.2 d
9					23.4 s	24.7 s	22.7 s	23.6 s
10					31.6 s	30.2 s	30.7 s	30.0 s
11	1.96/1.23	1.97/1.42		1.92/1.24	26.5 t	26.9 t	26.6 t	26.6 t
12	1.30	1.32/1.17		1.25	35.3 t	32.6 t	34.6*t	35.0 t
13					45.3 s	45.8 s	45.3 s	45.3 s
14					48.8 s	49.6 s	48.6 s	48.5 s
15	1.62	1.58	1.60	1.62	32.6 t	32.8 t	32.5 t	32.5 t
16	1.92/1.30	1.92/1.32		1.90/1.28 m	28.0 t	27.6 t	28.0 t	28.0 t
17	1.60	1.59	1.60	1.59	52.2 d	51.2 d	52.2 d	52.1 d
18	0.93 s	0.94 s	0.94 s	0.94 s	19.1 q	14.5 q	19.2 q	17.5 q
19	0.31/0.18 d	0.42/0.03 d	0.35/0.23 d	0.54/0.30 d	28.0 t	17.4 t	28.5 t	26.8 t
20	1.40	1.40		1.40	35.9 d	35.9 d	35.8 d	35.8 d
21	0.89	0.90		0.87	18.3 q	18.5 q	18.2 q	18.2 q
22	1.40	1.40		1.40	36.3 t	36.3 t	36.3 t	36.3 t
23	2.05/1.86	2.02/1.87		2.05/1.87	24.9 t	24.9 t	24.9 t	24.9 t
24	5.10 t, sept	5.09 t, sept	5.10 t, sept	5.08 t, sept	125.2 d	125.1 d	125.2 d	125.1 d
25					130.9 s	131.1 s	130.9 s	131.0 s
26	1.68 br s	1.68 br s	1.68 br s	1.68 br s	25.7 q	25.7 q	25.7 q	25.7 q
27	1.60 br s	1.60 br s	1.60 br s	1.60 br s	17.7 q	17.6 q	17.6 q	17.6 q
30	0.96 s	0.83 s	0.92 s	0.92 s	17.7 q	17.9 q	17.8 q	18.9 q
position	**11b**	**12b**	**13b**	**14b**	**11b**	**12b**	**13b**	**14b**
17	1.60	1.59		1.59	52.2 d	51.4 d	52.3 d	52.2 d
20	1.42	1.42		1.40	36.2 d	36.1 d	36.1 d	36.0 d
21	0.89	0.90		0.87	18.2 q	18.6 q	18.3 q	18.3 q
22	?	1.62/1.17		?	35.0 t	35.0 t	35.0 t	34.9 t
23	2.16/1.84	2.14/1.92		?	31.3 t	31.3 t	31.3 t	31.3 t
24					156.8 s	156.7 s	156.8 s	156.8 s
25	2.26	2.22		2.22	33.8 d	33.8 d	33.8 d	33.8 d
26	1.03 d	1.03 d	1.02 d	1.02 d	21.9*q	22.0 q	22.0*q	21.9 q
27	1.02 d	1.02 d	1.02 d	1.02 d	22.0*q	21.8 q	21.9*q	22.0 q
31	4.72/4.66 br s	4.72/4.66 br s	4.72/4.66 br s	4.71/4.65 br s	106.0 t	106.1 t	106.0 t	106.0 t

[a] For the exo-methylene series **11b**−**14b** only the values of the side chain (including position 17) are listed; all other ^{1}H and ^{13}C NMR chemical shifts are identical with the **a** series. All ^{1}H NMR resonances where no multiplicities are given, consist of nonresolvable multiplets due to overlap of resonances; the correct chemical shifts and the assignments were determined by 2D techniques. [b] Coupling constants—**11a**/**b**: J(2ax,3ax) = J(3ax,4ax) = 10.7 Hz, J(2eq,3ax) = J(3ax,4eq) = 4.4 Hz, J(4ax,4eq) = 11.2 Hz, J(5ax,6ax) = J(6ax,7ax) = 10.3 Hz, J(6ax,7eq) = 3.6 Hz, J(19,19) = 4.3 Hz; **12a**/**b**: J(2ax,3ax) = J(3ax,4ax) = 10.8 Hz, J(2eq,3ax) = J(3ax,4eq) = 4.4 Hz, J(4ax,4eq) = 12.1 Hz, J(4ax,5ax) = 12.0 Hz, J(7ax,8ax) = 8.0 Hz, J(7eq,8ax) = 1.7 Hz, J(19,19) = 5.5 Hz; **13a**/**b**: J(19,19) = 4.3 Hz; **14a**/**b**: J(2ax,3ax) = J(3ax,4ax) = J(4ax,5ax) = 10.0 Hz, J(2eq,3ax) = 5.4 Hz, J(5ax,6ax) = J(6ax,7ax) = 9.6 Hz, J(6ax,7eq) = 4.4 Hz, J(19,19) = 4.8 Hz. Side chains **11a**−**14a**: J(23,24) = 7.1 Hz, J(24,26) = J(24,27) = 1.0 Hz; **11b**−**14b**: J(25,26) = J(25,27) = 6.9 Hz. [c] * Interchangeable within the column. [d] Only clearly assigned ^{1}H NMR resonances are listed for **13a**/**b**; the ^{1}H NMR spectrum of the corresponding triacetate **14a**/**b** was much clearer due to less severe overlap, the structure elucidation was therefore performed via the latter compound. [e] Acetate resonances: OAc-3 1.99 s, OAc-4 1.95 s, OAc-6 1.99 s. [f] Acetate resonances: OAc-3 170.4 s and 21.0 q, OAc-4 170.2 s and 21.5 q, OAc-6 169.9 and 21.0. [g] Proton 4eq.

acetyloxymethyl group. Strong NOEs from the methoxy groups (OCH_3-3′, -3″) to the *meta*-coupled aromatic protons (H-2′, -2″) indicated two 3-methoxy-4-hydroxy-substituted benzene rings, and a NOE from H_2-3a to H_2-4a confirmed the relative cis orientation of the two methylene groups and their further substituents. Mutual NOEs between H-2 and H_2-3a indicated the close spatial proximity of these protons, which corresponds to a relative trans orientation of the 2-phenyl and the 3-acetyloxymethyl substituents. A value of $[\alpha]^{20}_D$ +17° for the specific rotation confirmed the absolute configuration of **10** as shown.[22] Taking into account all available data, compound **10** turned out to be the new (+)-acetyl ester of lariciresinol.[21,22]

Based on the available data, *Aglaia* species are mainly characterized by cycloartane-type triterpenes.[15,23−27] Moreover, dammarane-type triterpenes,[15,28,29] tirucallanes,[30] apotirucallanes,[31] and related protolimonoids (glabretals)[32] have also been isolated. The co-occurrence of structurally very similar cycloartanes and apotirucallanes in *A. argentea* Blume,[27,31] as well as dammaranes and a limonoid derivative in *A. elaeagnoidea* from Java,[15] suggests close biogenetic connections between the different structural types. In the leaves of *A. grandis* from Indonesia even the biogenetically more advanced C_{21}-pregnanes were shown to be accumulated together with cycloartane-type triterpenes.[26] From the leaf extract of *A. elaeagnoidea*, collected in Thailand, we have now isolated three inseparable pairs of 4-bis-norcycloartane-type triterpenes (or 14α-methylsterols) (**11a**+**b**−**13a**+**b**), which are very similar to the already-known structures of 4-dimethylated cycloartane triterpenes isolated from Indian collections of *A. elaeagnoidea* (syn. *A. roxburghiana*).[23,24] Each pair was shown to consist of a 24,25-dehydro- (**11a**−**13a**) and a 24-methylenecycloartane-based derivative (**11b**−**13b**), from which roxburghiadiol B (**11b**) has already been reported for the leaves and fruits of an Indian *A. elaeagnoidea*.[24] The

remaining five derivatives proved to be new compounds. The IR spectra of all derivatives were characterized by OH bands at 3590−3598 cm^{-1} and 3470−3472 cm^{-1} ($CHCl_3$) for **11a**+**b** and **13a**+**b**, and 3618 cm^{-1} (CCl_4) for **12a**+**b.** In this last pair, an additional keto function was indicated by the C=O frequency at 1702 cm^{-1}. Large amounts of the major pair (**13a**+**b**) could already be obtained by crystallization from the dry column fraction eluted with 30% EtOAc in hexane. From the corresponding mother liquor roxburghiadiol B (**11b**) was isolated, together with the new derivative **11a** by preparative TLC using $CHCl_3$−MeOH (97:3) as solvent. The remaining pair with a keto function (**12a**+**b**) was obtained from column fractions with 15% EtOAc in hexane and purified by TLC eluted with CH_2Cl_2−Et_2O (90:10).



On the basis of the ^1H NMR integration, one component in the pair **11a**+**b** was predominant with 80% (**11a**) over 20% of the higher homologue **11b**. A molecular formula of $C_{28}H_{46}O_2$ (HRMS) in combination with the NMR data for **11a** pointed toward a degraded triterpene with one double bond and a five-membered ring system, whereas **11b** differed by an additional CH_2 group (HRMS). The ^1H NMR spectrum of **11a**+**b** showed one olefinic triplet at δ 5.08 with an intensity of 0.8, accompanied by a smaller exomethylene-type resonance with two broad singlets at δ 4.70 and 4.64, with an intensity of 0.2 each. Two secondary hydroxyl groups were indicated by a dddd at δ 3.68 and a ddd at δ 3.08, both showing two large ax−ax coupling constants typically for an axial H and an equatorial OH in a cyclohexane ring system. The intensities of the H_{ax} resonances were equivalent to 1.0 H each. This implies that these protons are within a subunit of the molecule identical for both homologues. The same is true for the two most characteristic resonances at δ 0.29 and 0.16 (two doublets of intensity 1.0, J = 4.8 Hz). Chemical shifts and couplings of these protons were typical for cyclopropane protons. All these data were compatible with triterpenes of the cycloartenol-type, which are characterized by an additional cyclopropane ring at C-9 and C-10 in the B-ring. However, the two geminal methyl groups at C-4 (CH_3-28 and CH_3-29) were missing. Two 4-bis-norcycloartanediols have already been reported for an Indian collection of *A. elaeagnoidea* (= *A. roxburghiana*), of which one is identical with our compound **11b** and was designated as roxburghiadiol B.[24] The predominant compound **11a** (80% purity) proved to be a new compound; the only difference from **11b** was evident in the C-17 side chain, which carries no exomethylene group.

The ^1H and ^{13}C NMR spectra for compounds **11a**+**b**−**13a**+**b** are listed in Table 1. For the exomethylene series (**11b**−**13b**), which constituted 20% of the pair **11**, ca. 50% of **12**, and ca. 30% of **13**, only the differing resonances for C-17 through C-31 (^1H NMR and ^{13}C NMR) are listed separately, because all other signals were identical for both series. For roxburghiadiol B (**11b**) the assignments for the protons and carbon atoms at positions C-2 and C-12 had to be reversed (cf. Balakrishna et al.[24]). The

Table 2. ^1H NMR Data for Flavaglines **15**−**17** (250 MHz, $CDCl_3$, δ/ppm, TMS, JHz)

position	**15**	**16**	**17**
1	4.97 (d, 6.5)	6.02 (d, 5.2)	4.99 (d, 6.4)
2	3.89 (dd, 14.3, 6.5)	4.05 (dd, 14.3, 5.2)	3.87 (dd, 14.3, 6.4)
3	4.31 (d, 14.3)	4.47 (d, 14.3)	4.32 (d, 14.3)
5	6.32 (s)	6.29 (s)	6.34 (s)
2′	7.09 (d, 8.8)	7.07 (d, 8.7)	6.52 (d, 2.2)
3′	6.67 (d, 8.8)	6.62 (d, 8.7)	
5′	6.67 (d, 8.8)	6.62 (d, 8.7)	6.70 (d, 8.5)
6′	7.09 (d, 8.8)	7.07 (d, 8.7)	6.86 (dd, 8.5, 2.2)
2″,6″	6.87 (dd, 7.4, 2.0)	6.96 (dd, 7.4, 1.9)	6.87 (dd, 7.5, 2.0)
3″,4″,5″	7.00−7.08 (m)	7.00−7.07 (m)	7.07 (m)
OCH_3-8	4.11 (s)	3.98 (s)	4.12 (s)
OCH_3-3′			3.80 (s)
OCH_3-4′	3.71 (s)	3.68 (s)	3.60 (s)
$COOCH_3$	3.65 (s)	3.63 (s)	3.66 (s)
$OCOCH_3$		1.91 (s)	
OCH_2O	5.90 (s)	5.89 (d, 1.1) 5.87 (d, 1.1)	5.91 (s)

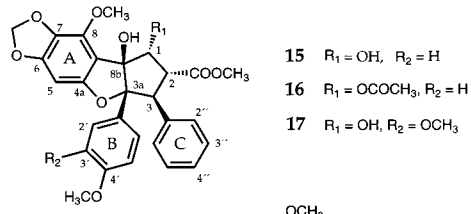
^1H and ^{13}C NMR assignments were obtained unambiguously by extensive use of 2D NMR techniques including H−H COSY, C−H COSY, NOESY, and CH long-range correlation.

The ^1H and ^{13}C NMR spectra of **12a**+**b** were very similar to those of **11a**+**b**. Only one secondary hydroxy group, however, was present in **12** (dddd at δ 3.67 for 3-H), and an additional ketonic carbon resonance at δ 212.2 appeared in the ^{13}C NMR spectrum. The molecular formula of $C_{28}H_{44}O_2$ is in favor of an oxidation product of **11a**+**b** with the transformation of one hydroxyl group to an oxo function. The position of this oxo group at C-6 was clearly derived from the connectivities in the 2D NMR spectra. A second difference in **12** is the ratio of the homologues, which was about 1:1 for **12a**:**12b**. This followed clearly from the integration of the olefinic open-chain proton H-24 in the case of **12a** and the exomethylene signals in the case of **12b**. The third difference is somewhat surprising: the ^{13}C NMR resonance for the cyclopropane carbon atom was found at δ 17.4 and not in the usual region of about δ 27−30. On the other hand, a series of glucosides of related pentacyclic hydroxytriterpenes has been described from *Dysoxylum cumingianum* C. DC. (Meliaceae), wherein the cyclopropane methylene bridge between C-13 and C-14 (rings C/D) is characterized by ^{13}C NMR chemical shifts of δ 16.7−17.9.[33] A similar 13,14-cyclopropane derivative has also been isolated from *A. tomentosa* (syn. *A. ferruginea* C. T. White & Francis).[32] In that paper, ^{13}C NMR data were listed but no assignments given. To support the structures of **12a**+**b** unambiguously, all 2D methods mentioned above were used for clarification. Despite the unusual ^{13}C NMR chemical shift, the 9,10-methylene bridge position at ring B could be confirmed. The C/H long-range correlation data were absolutely clear: strong cross peaks for C-1→ H-19, C-5 → H-19, C-9 → H-19, and C-10 → H-19 are only compatible with the cyclopropane ring attached at the B ring at C-9 and C-10. So the reason for the remarkable difference in the chemical shift for the cyclopropane C-19 signal in the 6-oxo compound **12** versus **11**, **13**, and **14** ($\Delta\delta$ ca. 10 ppm) needs to be explained. The anisotropic effect of the C-6 carbonyl group cannot explain fully the observed large shift effect. One possible reason may be that the sp^2 hybridization of C-6 results in a conformational change (flattening) in this part of the molecule. The ^{13}C NMR chemical shift of C-19 seems to be most sensitive to this change of conformation.

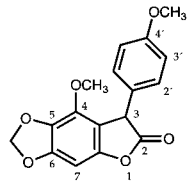
The pair **13a**+**b** is also closely related to **11a**+**b** and **12a**+**b**. The molecular formula $C_{28}H_{46}O_3$ (HRMS) for the predominant lower homologue **13a** is in accord with a trihydroxy derivative. This was confirmed by the NMR data with three −CHOH− elements: three multiplets in the region δ 3.50−3.55 in the ^{1}H NMR spectrum and three carbon resonances in the region δ 72−81 in the ^{13}C NMR spectrum. Due to severe overlap in the ^{1}H NMR spectrum of **13a**+**b**, the further structure elucidation was based on data of the more easily accessible triacetates **14a**+**b**. In the latter case, the protons geminal to OAc were well resolved and all coupling constants could be obtained. The resonance at δ 4.90 (H_{ax}-3) was a ddd with two ax−ax-type couplings, one to H_{ax}-2 and one to −CH_{ax}OAc at δ 5.07, and one ax−eq coupling to H_{eq}-2. The dd at δ 5.07 (H_{ax}-4) showed two ax−ax couplings, one to H_{ax}-3 and the other one to the axial bridge proton H_{ax}-5. This proton also showed an ax−ax coupling to the third −CH_{ax}OAc at δ 4.60 (H_{ax}-6), which appeared as a ddd with two ax−ax couplings to H_{ax}-5 and H_{ax}-7, and one ax−eq coupling to H_{eq}-7. The necessary identification of the protons followed clearly from C−H COSY and C−H long-range correlation. The coupling data outlined above are conclusive for the sequence −CH_2−CHOAc−CHOAc−CH (bridge)−CHOAc−CH_2− with oxygenations at the equatorial positions of C-3, C-4, and C-6. The two components of the biogenic pair **13a**+**b** are therefore the two side-chain homologues of the 3,4,6-trihydroxy derivative of 4-bisnorcycloartane.

From the phytochemical literature on plants in the family Meliaceae, aromatic compounds with a cyclopenta[*b*]benzofuran skeleton represent a typical chemical character of the genus *Aglaia*.[6,7,34−36,47,48] They appear to be responsible for the pronounced insecticidal activity of many different species.[5] In contrast to the more widely distributed nitrogen-containing compounds of the rocaglamide type,[6,7] none of the cyclopenta[*b*]benzofuran derivatives from *A. elaeagnoidea* described in the present paper contains nitrogen. Together with different substitution patterns they represent a new series with highly insecticidal activities. With respect to the already-known molecular structures of aglains from *A. argentea* and the co-occurrence of aglaforbesins and forbaglins with rocaglaol in *A. forbesii* King, the cyclopenta[*b*]benzofuran skeleton appears to be derived from a flavonoid nucleus linked with a cinnamic acid moiety.[34] Consequently, the incorporation of nitrogen into rocaglamide represents a late biosynthetic step, and hence, the general use of the term *rocaglamides* for all derivatives of that basic structure can no longer be justified. Regarding the restricted occurrence of this type of cyclopenta[*b*]benzofurans to the genus *Aglaia* and the incorporation of a flavonoid moiety as a central biosynthetic step, we therefore suggest naming this class of compounds flavaglines.

From the lipophilic leaf, stem, and root bark extracts of *A. elaeagnoidea* we isolated three compounds with a cyclopenta[*b*]benzofuran skeleton (**15**−**17**). The UV spectra were characterized by a maximum at 298 nm and a shoulder at 228 nm (MeOH), together with a less-pronounced shoulder at 285 nm in compounds **15** and **16,** and vice versa with λ_{max} at 285 nm and a distinct shoulder at 298 nm in **17**. From the IR spectra of all compounds, an ester function could be deduced from the carbonyl band at 1754 cm^{-1} (CCl_4), which was especially pronounced in compound **16**. Additional OH groups were indicated by two bands at 3582 and 3543 cm^{-1} for **15** and **17**, and one at 3575 cm^{-1} for **16**.



15 R_1 = OH, R_2 = H
16 R_1 = $OCOCH_3$, R_2 = H
17 R_1 = OH, R_2 = OCH_3



18

The ^{1}H NMR data of compound **15** showed some relation with those of rocaglamide;[37] however, the resonances of two parts of the molecule showed characteristic differences. The first one concerned the cyclopentane ring resonances for H-1, H-2, and H-3, which deviated from the rocaglamide values but agreed very well with the data described for methyl rocaglate,[37] previously named aglafolin,[47] where the amide moiety is replaced by a methyl ester group. This agreed also with the C=O band observed in the IR spectrum and the ester methoxy group at δ 3.65 (Table 2). A second difference from both rocaglamide and methyl rocaglate could be observed for the aromatic ring protons. Compared to these compounds, the resonances for the aromatic OMe-6 and H-7 were missing and were replaced by a methylenedioxy signal (singlet for 2H at δ 5.90). Only one aromatic proton resonance remained as a singlet at δ 6.32 (in the spectrum of methyl rocaglate H-5 appeared as a doublet at δ 6.29 with a *meta* coupling of 2.4 Hz).

Analysis of the chemical shift values of the three methoxy groups was in favor of the OCH_2O bridge being at C-6, C-7. According to the literature, the *para*-OMe-4′ of ring B is always found close to δ 3.70[37] (independent proof by NOE OCH_3-4′→H-3′/H-5′). The chemical shift of δ 3.65 was characteristic for an ester OMe group.[37] The third methoxy resonance at δ 4.11, therefore, belongs to the A ring; it showed a downfield shift compared to the OMe-8 resonance of rocaglamide at δ 3.84. This downfield shift is typical for an additional adjacent oxygen atom (O-7 of the 6,7-methylenedioxy group). Independent proof was furnished by reversed long-range C−H COSY giving all expected cross peaks for the substitution pattern proposed.

Concerning the A ring, the proton at δ 6.32 gave very strong cross peaks with four carbon atoms (C-6, C-7, C-4a, C-8a), the fifth one (C-8), carrying the methoxy group at δ 4.11, showed a very weak and hardly detectable cross peak. This indicated a *para* position of the OCH_3 group relative to the proton of the A ring. Because only positions C-5 and C-8 are suited for a *para* relationship, the only possible sites for the methylenedioxy bridge are positions C-6 and C-7.

The remaining question, whether the methoxy group is attached to positions C-5 or C-8 can be answered either by biochemical considerations or NMR evidence. In view of the numerous phloroglucinol-derived flavaglines,[6,7,34−36,47,48] a 8-methoxy-6,7-methylenedioxy substitution is much more likely than a 5-methoxy-6,7-methylenedioxy substitution, which would change the whole system. The former substitution pattern with a 4a,6,7,8-tetraoxygenated A ring is also strongly supported by the ^{13}C NMR chemical shifts of this aromatic ring system. Comparison of the shift data of compound **15** with the corresponding values for a 4a,6,8-trioxygenated A ring (e.g., in aglaiastatin[45] where the resonances have been completely assigned) gave the ex-

pected substituent shifts for an additional oxygenation at C-7: C-6 and C-8 showed the effect of an additional *ortho*-oxygen (164.0[45] → 152.3, $\Delta\delta = -11.7$ ppm and 157.5 → 139.4, $\Delta\delta = -18.1$ ppm, respectively), C-5 and C-8a with a *meta* relationship to C-7 showed only small effects (89.4 → 88.5, $\Delta\delta = -0.9$ ppm and 107.2 → 110.2, $\Delta\delta = +3.0$ ppm), and C-4a showed a typical *para*-oxygen shift (161.1 → 154.2, $\Delta\delta = -6.9$ ppm). In the case of a 4a,5,6,7-tetraoxygenated compound, matters should be entirely different. Especially the extremely high-field shifted ^{13}C NMR doublet for the only aromatic CH unit in ring A needs the maximal upfield shifting effect of two *ortho* plus one *para*-oxygen to explain the unusual aromatic chemical shift value of δ 88.5. However, this requirement is only fulfilled in the 8-methoxy- and not in the 5-methoxy-6,7-methylenedioxy derivative. The ^1H and ^{13}C NMR chemical shift data together with C−H long-range correlation are, therefore, only compatible with a 8-methoxy-6,7-methylenedioxy substituted A ring. The combination of C−H COSY and long-range C−H COSY allowed an unambiguous assignment of all resonances in the ^1H and ^{13}C NMR spectra and furnished additional proof for the connectivities in the proposed structure **15** (see Table 2 and Experimental Section). The FDMS of compound **15** showed a molecular mass of 506; HRMS agreed with the postulated formula, $C_{28}H_{26}O_9$.

The relative and absolute stereochemistries of rocaglamide are well known from single-crystal X-ray analysis and enantioselective synthesis.[35,38] The NOE data for irradiation at the three protons of the cyclopentane ring of compound **15** (H-1 → H-2, H-2 → H-1, H-2′, H-2″, and H-3 → H-2″) agreed perfectly with the relative stereochemistries described for rocaglamide and all related derivatives. Moreover, the optical rotation of $[\alpha]^{20}_D$ −50° was also compatible with the described absolute stereochemistries of this type of compounds isolated from different *Aglaia* species.

All flavaglines isolated from *A. elaeagnoidea* are characterized by a 8-methoxy-6,7-methylenedioxy-substituted ring A and a methyl ester group at C-2 instead of the more widespread amide type. Although derivatives of the ester type have already been reported for *A. odorata*,[37,39,43] *A. elaeagnoidea* (from Java),[15] *A. rimosa* (Blanco) Merr. (syn. *A. elliptifolia* Merr.),[47] and *A. elliptica*,[48] the characteristic substitution of the A ring seems to be less common. In the latter species, four derivatives have been described with a 3′,4′-methylenedioxy group in the B ring; however, all deviate by having a 6,8-dimethoxy substituted A ring.[48] Concerning the 8-methoxy-6,7-methylenedioxy group in ring A, three derivatives (aglaroxins A−C) have already been described in a recent patent for the bark of a Sri Lankan collection of *A. elaeagnoidea* (syn. *A. roxburghiana*);[40] however, all belong to the amide type. In this patent, the UV data, the molecular masses (FD and/or FAB), and the ^{13}C NMR data (in $CDCl_3$) were listed. Although the NMR shifts were not assigned, the listed values fitted very well with our data for the 8-methoxy-6,7-methylenedioxy-substituted ring A of compounds **15**−**17**. These were named pannellin (**15**), pannellin 1-*O*-acetate (**16**), and 3′-methoxypannellin (**17**).[41]

Pannellin 1-*O*-acetate (**16**) was shown to be an acetylation product of **15** with a specific rotation of $[\alpha]^{20}_D$ −65°. The transformation of OH-1 to $OCOCH_3$-1 was indicated by the additional acetyl resonance in the ^1H NMR spectrum with a singlet at δ 1.91, as well as by the downfield shift of 1-H from δ 4.97 in **15** to δ 6.02 in **16** (typical "acetyl-shift"). The molecular mass of *m*/*z* 548.1683 for $C_{30}H_{28}O_{10}$ and the prominent M-60 fragment at *m*/*z* 488 (loss of acetic acid[39]) confirmed the proposed structure.

3′-Methoxypannellin (**17**) ($[\alpha]^{20}_D$ −45°) is also closely related to pannellin (**15**), the only difference being an additional OCH_3-3′ group on the B ring. The symmetrical ^1H NMR resonance pattern for the AA′BB′ system of the *para*-substituted B ring of compound **15** changed to an ABC pattern of 3H with one *ortho* coupling, one *meta* coupling, and one *ortho* and *meta* coupling proton in the case of compound **17** (see Table 2). The chemical shifts and the coupling pattern agreed with a 3′,4′-dimethoxyphenyl substituent.

The IR spectrum of compound **18**, isolated as a minor constituent from the leaf extract of *A. elaeagnoidea*, showed many similarities with the pannellins (**15**−**17**); however, it differed clearly by two very strong bands at 1775 and 1248 cm^{-1}, indicative of a different type of ester. The UV spectrum also differed by exhibiting characteristic λ_{max} at 304, 268, and 235 nm. From the ^1H and ^{13}C NMR data it became clear that in compound **18** only some partial structures typical for flavaglins are present, namely, the methylenedioxy-containing phloroglucinol-derived aromatic system and the *p*-methoxyphenyl substituent. According to HRMS, the molecular formula is $C_{17}H_{14}O_6$, which leaves only a CH and a CO fragment (incorporated in a ring system) in addition to the other units outlined above. The appearance of a lactone carbonyl singlet in the ^{13}C NMR spectrum at δ 167.9 was unambiguously in favor of a lactonic five ring with the carbonyl function at C-2 and a CH(ArOMe) rest at C-3. The IR carbonyl band at 1775 cm^{-1} agreed also with a five-ring lactone (usual values 1760−1780 cm^{-1}). A reverse arrangment with CH(ArOMe) at C-2 and the carbonyl at C-3 would better match the corresponding partial structure of the flavaglins; however, the resulting keto carbonyl is not compatible with the ^{13}C NMR data. Furthermore, the ^1H NMR data of a synthetic five-ring ketone[40] of this type were also different from our data (H-3 for compound **18** at δ 6.11, versus 5.38 in the case of the corresponding 2-aryl-3-oxo-compound).[40] Further proof of the lactone structure **18** by NOE was not possible, because the OCH_3-4 group was rotated away from the aryl substituent (no NOE OCH_3-4 → 2′-H/6′-H was detectable). Compound **18**, designated as aglalactone, obviously belongs to the same class of secondary metabolites as the pannellins (**15**−**17**). The question of whether it has the same biogenetic precursors, however, cannot be answered.

As shown in Table 3, pannellin (**15**) and pannellin 1-*O*-acetate (**16**) exhibited the strongest toxicity toward neonate larvae of the polyphagous pest insect *S. littoralis*, whereas for the structurally similar aglalactone (**18**) no significant effect was observed. Insufficient quantities of 3′-methoxypannellin (**17**) precluded bioassay. In accordance with the data already published for the corresponding nitrogen-containing flavaglines ("rocaglamides"),[6,7] the acetylation of the hydroxy group at position C-1 in pannellin 1-*O*-acetate (**16**) leads to a reduction in insecticidal activity. None of the other new compounds showed any toxicity to insects (Table 3). This is in agreement with a previous investigation using *Peridroma saucia* (variegated cutworm), wherein neither bisamides nor dammarane triterpenes were shown to be active.[43] Compared with azadirachtin as a positive control against *S. littoralis*, pannellin (**15**) turned out to be one of the most active flavagline obtained so far from an *Aglaia* species, with a LC_{50} value of 2.1 μg/g artificial diet compared with 6.1 μg/g for azadirachtin (Table 3, cf. Nugroho et al.[6,7] and Ishibashi

Table 3. Insecticidal and Growth Inhibitory Activities of the Novel Compounds from *Aglaia* Species[a]

	Lymantria dispar	*Spodoptera littoralis*	
compound	growth inhibition EC_{50} (95% FL[b]) μg/g fr.wt	survival rate LC_{50} (95% FL[b]) μg/g fr.wt	growth inhibition EC_{50} (95% FL[b]) μg/g fr.wt
piriferinol (**5**)		>250	>250
edulimide (**7**)		>250	>250
laricresinol acetate (**10**)		>250	>250
triterpene (**11a**+**b**)		>250	>250
triterpene (**12a**+**b**)		>250	>250
triterpene (**13a**+**b**)		>250	>250
pannellin (**15**)	1.4 (0.5−11.0)	2.1 (1.2−4.3)	0.24 (0.20−0.29)
pannellin 1-*O*-acetate (**16**)		12.2 (9.6−19.8)	1.2 (1.1−1.3)
aglalactone (**18**)		>100	>100
azadirachtin[c]	0.6 (0.3−1.2)	6.1 (4.1−11.0)	0.11 (0.05−0.17)

[a] Neonate larvae of *S. littoralis* ($n = 20$) were reared on bean-based diet (3.8 g), and those of *L. dispar* ($n = 10$) on wheat germ−casein-based artificial diet (3.6 g). Both diets were spiked with various concentrations of test compounds. After 5 days, survival rate and growth inhibition of *S. littoralis* were determined in triplicate and compared to controls. The experiments with *L. dispar* were performed for 8 days. In each case, LC_{50} and EC_{50} was determined by probit-log analysis. [b] FL = Fiducial limits. [c] Positive control.

et al.[37]). The growth rate of even the bigger and less sensitive larvae of *L. dispar* (gypsy moth) was significantly reduced and resulted in an EC_{50} value as low as 1.4 μg/g (Table 3).

In a recent taxonomic treatment of the genus *Aglaia* by C. M. Pannell, a wide species concept was adopted where, in many species, even the most indicative morphological characters like the indumentum, fruits, and flowers, show considerable variation.[44] Future work will have to demonstrate whether a division of these highly variable species into separate species or subspecies may be justified. With respect to the very characteristic bisamides and flavaglines known so far only from *Aglaia* species, together with the more widely distributed triterpenes and lignans as well as other constituents, a significant taxonomic contribution can also be expected from phytochemical characters. However, bearing in mind that secondary compounds may have crucial ecological functions, chemical variation can also be environmentally induced, and hence, for any systematic conclusion, such variations have to be interpreted more carefully. On the other hand, many biological activities can often be derived only from slight variations of less or even inactive basic structures, and therefore, it appears worthwhile to gain more insight into the overall biogenetic capacity of the genus. That can be attained by a comprehensive phytochemical screening, comparing not only different species and provenances, but also different individuals of the same population as well as their different organs. With regard to the activities already known from phytochemicals isolated from *Aglaia* species,[7,12−14,27,45−48] a more detailed screening of different provenances, even if the corresponding species have already been investigated, may also provide new and potential lead structures for a broad range of practical uses. This may be underlined by a more recent report on a Thai collection of *A. elliptica*, in which several of novel cytotoxic flavaglines were isolated as major components,[48] which have not been found in a previous investigation of an Indonesian collection.[7]

Experimental Section

General Experimental Procedures. Optical rotation, Perkin−Elmer polarimeter 241; UV, Hewlett−Packard, 8452A diode array spectrophotometer; IR, Perkin−Elmer 16PC FT-IR; NMR, Bruker, AM 400 WB and AC 250; MS, Finnigan MAT 900 S; HPLC, Hewlett−Packard 1090 II, UV diode array detection at 230 nm, column 250 × 4 mm, Hypersil BDS C-18, 5 μm, mobile phase MeOH (gradient 60−100%) in aqueous buffer (0.015 M *o*-phosphoric acid, 0.0015 M tetrabutylammonium hydroxide, pH 3), flow rate 1 mL/min.

Plant Material. Leaves, stem, and root bark from different individuals of *Aglaia* species were collected separately: (a) *A. elaeagnoidea* from Khao Soi Dao, near Chantaburi (southeast Thailand), three individuals (HG14, HG16, HG18, February 1997) and from the Kasetsart Forest Research Station near Trat (southeast Thailand), two individuals (HG4, HG5, July 1996); (b) *A. silvestris* from Khao Soi Dao, near Chantaburi (southeast Thailand), one individual (HG15, February 1997); (c) *A. grandis* from Khao Cha Mao, near Rayong (southeast Thailand), one individual (HG19, August 1996); (d) *A. tomentosa* from Maxwell Hill (Malaysia), one individual (HG3, February 1996); (e) *A. edulis* from Khao Kitchakut, near Chantaburi (southeast Thailand), one individual (HG12, August 1996). Voucher specimens are deposited at the Herbarium of the Institute of Botany, University of Vienna (WU).

Extraction and Isolation. Dried parts of *Aglaia* species were ground and extracted with MeOH at room temperature for 3 days, filtered, and concentrated. The aqueous residue was extracted with $CHCl_3$. The $CHCl_3$ fractions were evaporated to dryness and roughly separated by column chromatography (Merck Si gel 60, 35−70 mesh) and further by preparative MPLC (400 × 40 mm column, Merck LiChroprep silica 60, 25−40 μm, UV detection, 254 nm) as well as by column chromatography with Sephadex LH-20 in MeOH. Preparative TLC (Merck, Si gel 60, 0.5 mm) was used to finally purify the compounds. Cycloartane nortriterpenes were detected with anisaldehyde−H_2SO_4−HOAc spray reagent in MeOH (modified after Stahl[49]).

Compounds 5, 11a+b, 12a+b, 13a+b, 16, and 18. A portion (3 g) of the $CHCl_3$ fraction from 157 g of dried leaves of *A. elaeagnoidea* of the combined individuals HG4 and HG5 from Trat together with HG16 from Khao Soi Dao was separated roughly by column chromatography (Si gel). Elution with 30% EtOAc in hexane yielded, after crystallization from Et_2O−CH_2Cl_2, 138 mg of **13a**+**b**. The fractions eluted with 15% EtOAc in hexane contained **12a**+**b**, **16**, and **18**, which were further purified by MPLC with 15% EtOAc in hexane and TLC using 10% Et_2O in CH_2Cl_2 to give 45 mg of **12a**+**b**, 2 mg of **16**, and 3 mg of **18**. The fractions eluted with 30% EtOAc in hexane were purified with TLC using 3% MeOH in $CHCl_3$ to give 55 mg of **11a**+**b**. The fractions eluted with 100% EtOAc followed by TLC with 3% MeOH in $CHCl_3$ led to the isolation of 4 mg of **5**.

Compound 7. A portion (670 mg) of the $CHCl_3$ fraction from 11 g of dried leaves of *A. edulis* (HG12) was separated roughly with Si gel chromatography. The fractions eluted with MeOH were further purified with Sephadex LH-20 and TLC with 4% MeOH in $CHCl_3$ to yield 4 mg of **7**.

Compound 10. A portion (1040 mg) of the $CHCl_3$ fraction from 63 g of dried leaves of *A. elaeagnoidea* (HG18) were separated roughly with Si gel chromatography. The fractions eluted with 30% EtOAc in hexane were further purified by MPLC with the same solvent to yield 7 mg of **10**.

Compound 15. A portion (220 mg) of the $CHCl_3$ fraction from 16 g of dried root bark of *A. elaeagnoidea* (HG14 + HG18) was separated roughly by column chromatography (Si gel). The fractions eluted with 15% and 30% EtOAc in hexane were combined and further separated by MPLC with 15% EtOAc in hexane affording 7 mg of **15**.

Compound 17. A portion (360 mg) of the $CHCl_3$ fraction from 99 g of dried stem bark of *A. elaeagnoidea* (HG14, HG16, HG18) was separated roughly by column chromatography (Si gel). The fractions eluted with 30% EtOAc were further purified by MPLC with 30% EtOAc in hexane and TLC with 20% Et_2O in CH_2Cl_2 to yield 1 mg of **17**.

Insect Bioassays. Larvae of *S. littoralis* were from a laboratory colony reared on a bean-based artificial diet.[50] The chronic feeding bioassays were conducted with freshly hatched larvae ($n = 20$) that were kept on artificial diet spiked with different concentrations of the test compounds (0.1 μg − 100 μg/g fresh wt) dissolved in Me_2CO. After 5 days (moist chamber, 29 °C, darkness) the survival and weight of larvae were determined in comparison to the control group treated with the carrier only. Larvae of *L. dispar* were from a laboratory colony reared on a wheat germ−casein-based diet.[51] Bioassays were conducted with freshly hatched larvae ($n = 10$), kept on diet spiked with 1 μg − 100 μg/g fresh wt of test compounds. After 8 days (moist chamber, 26 °C, darkness) mean weight of surviving larvae in comparison to controls was determined. Commercial azadirachtin (>96%) from Roth (Karlsruhe, FRG) was used as a positive control. From the dose-response curves in each experiment (three replicates), LC_{50} and EC_{50} values were calculated by probit-log analysis.

Piriferinol [*N*-Cinnamoyl-2-(2-hydroxy-2-methylpropanoylamino)-pyrrolidine] (5): $[\alpha]^{20}_D$ +8° (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 284 (4.16) nm; IR ($CHCl_3$) ν_{max} 3406 m, 2954 m, 2926 s, 2854 m, 1672 s, 1650 s, 1602 s, 1578 w, 1506 s, 1452 m, 1410 s, 1324 w, 1262 w, 1172 m, 1156 w, 1118 w, 990 w, 980 w, 918 w cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.67 (d, 1H, $J = 15.4$ Hz, H-3″), 7.54 (m, 2H, H-5″, -9″), 7.35 (m, 3H, H-6″, -7″, -8″), 7.26 (br d, 1H, $J = 7$ Hz, NH), 6.93 (d, 1H, $J = 15.4$ Hz, H-2″), 6.11 (br dd, 1H, $J = 7$, 7 Hz, H-2′), 3.77 (m, 1H, Hα-5′), 3.54 (m, 1H, Hβ-5′), 2.28 (m, 1H, Hβ-3′), 1.98 (m, 3H, Hα/Hβ-4′ and Hα-3′), 1.46 (s, 3H, Me-3), 1.35 (s, 3H, Me-4); FDMS *m/z* 302 (M^+, $C_{17}H_{22}N_2O_3$); EIS (70 eV) *m/z* 302 (3, M^+), 215 (16, M^+ − hydroxymethylpropanoyl), 199 (32, 215 − NH_2), 131 (73, cinnamoyl$^+$), 103 (35, 131 − CO), 85 (38), 71 (42), 57 (100).

Edulimide [N_1-Cinnamoyl-N_2-acetyl-N_2-dihydrocinnamoyl-putrescine] (7): UV (MeOH) λ_{max} (log ϵ) 282 (3.91) nm; IR ($CHCl_3$) ν_{max} 3450 w, 3350 br, 2930 m, 2858 w, 1664 s, 1646 s, 1598 m, 1580 m, 1526 s, 1486 m, 1454 m, 1432 m, 1376 w, 1352 w, 1304 w, 1190 w, 1124 w, 978 w cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94 (dd, 2H, $J = 8.0$, 1.3 Hz, H-5″, -9″), 7.75 (d, 1H, $J = 15.1$ Hz, H-3″), 7.35−7.55 (m, 8H, H-5−H-9, H-6″−H-8″), 6.85 (d, 1H, $J = 15.1$ Hz, H-2″), 5.67 (v br s, 1H, H−N1′), 3.62 (m, 2H), 3.46 (m, 4H), and 3.30 (m, 2H) (4 × 2H, H_2-2, -3, -2′, -5′), 1.96 (s, 3H, $NCOCH_3$), 1.77 (m, 2H) and 1.62 (m, 2H) (2 × 2H, H_2-3′, -4′);^{13}C NMR ($CDCl_3$) δ 141.2 (d, C-3″), 129.9, 128.4, 127.7, 127.2, 126.9, and 126.0 (6 × d, C-5−C-9 and C-5″−C-9″), 117.0 (d, C-2″), 46.2 (correlating to ^1H resonance at 3.46), 42.2 (corr. to 3.62), 37.2 (corr. to 3.30), and 35.1 (corr. to 3.46) (4 × t, C-2, C-3, C-2′, C-5′), 26.0 (corr. to 1.77) and 25.7 (corr. to 1.62) (2 × t, C-3′, C-4′), 21.2 (q, acetyl CH_3); FDMS *m/z* 392 (M^+, $C_{24}H_{28}N_2O_3$); EIMS (70 eV) *m/z* 392 (4, M^+), 349 (14, M^+ − acetyl), 290 (55), 169 (72), 131 (100, cinnamoyl$^+$), 103 (72, 131 − CO).

(+)-Methylarctigenin [(+)−(2*S*,3*S*)-2,3-*bis*(3,4-Dimethoxybenzyl)-butanolide] (8): $[\alpha]^{20}_D$ +32° (*c* 0.5, $CHCl_3$), {lit.[19,20] $[\alpha]^{20}_D$ −32.3° for biogenic material and +32.3° for the synthetic optical antipode};[20] ^1H NMR, ^{13}C NMR, and EIMS agreed fully with Chimichi et al.[19]

(+)-Lariciresinol 3-acetate [3-Acetyloxymethyl-4-(4-hydroxy-3-methoxybenzyl)-2-(4-hydroxy-3-methoxyphenyl)-tetrahydrofuran] (10): $[\alpha]^{20}_D$ +17° (*c* 0.3, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 282 (3.79), 230 (4.11) nm; IR (CCl_4) ν_{max} 3556 m, 3004 w, 2960 w, 2938 w, 2854 w, 1744 s, 1614 w, 1514 s, 1464 m, 1452 w, 1432 w, 1368 m, 1268 s, 1236 s, 1206 m, 1186 w, 1152 m, 1122 w, 1038 m, 856 w cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.88 (d, 1H, $J = 8.0$ Hz, H-5′), 6.85 (d, 1H, $J = 1.9$ Hz, H-2′), 6.84 (d, 1H, $J = 8.2$ Hz, H-5″), 6.80 (dd, 1H, $J = 1.9$, 8.0 Hz, H-6′), 6.67 (dd, 1H, $J = 8.2$, 2.0 Hz, H-6″), 6.66 (d, 1H, $J = 2.0$ Hz, H-2″), 5.58 and 5.50 (2 × br s, 2 × 1H, OH-4′, -4″), 4.76 (d, 1H, $J = 6.3$ Hz, H-2), 4.35 (dd, $J = 11.2$, 7.0 Hz, Hα-3a), 4.17 (dd, 1H, $J = 11.2$, 7.3 Hz, Hβ-3a), 4.06 (dd, 1H, $J = 8.6$, 6.4 Hz, Hα-5), 3.89 and 3.88 (2 × s, 2 × 3H, OCH_3-3′, -3″), 3.72 (dd, 1H, $J = 8.6$, 6.4 Hz, Hβ -5), 2.84 (dd, 1H, $J = 12.9$, 4.7 Hz, Hα-4a), 2.72 (m, 1H, H-4), 2.55 (m, 1H, H-3), 2.53 (dd, 1H, $J = 12.9$ Hz, Hβ-4a), 2.01 (s, 3H, acetyl CH_3); ^{13}C NMR ($CDCl_3$) δ 170.9 (s, C=O), 146.6 (s, C-3′), 146.5 (s, C-3″), 145.1 (s, C-4′), 144.1 (s, C-4″), 134.3 (s, C-1′), 131.9 (s, C-1″), 121.1 (d, C-6″), 118.8 (d, C-6′), 114.5 (d, C-5″), 114.2 (d, C-5′), 111.2 (d, C-2″), 108.3 (d, C-2′), 83.1 (d, C-2), 72.7 (t, C-5), 62.7 (t, C-3a), 55.94 and 55.92 (2 × 5q, 3′− and 3″−CH_3), 49.0 (d, C-3), 42.5 (d, C-4), 33.3 (t, C-4a), 20.8 (acetyl CH_3); EIMS (70 eV) *m/z* 402 (97, M^+), 342 (18, M^+ − HOAc), 219 (42), 205 (67), 190 (33), 151 [87, $C_6H_3(OH)(OCH_3)-CHO^+$], 137 [100, $C_6H_3(OH)(OCH_3)-CH_2+$], 94 (13), 55 (15); HREIMS *m/z* 402.1680 (calcd for $C_{22}H_{26}O_7$, 402.1679).

28,29-*bis*-Norcycloarten-3β,6α-diol (11a) (80%) and Roxburghiadiol B[24] [24-Methylene-28,29-*bis*-norcycloartan-3β,6α-diol] (11b) (20%): IR ($CHCl_3$) ν_{max} 3598 w, 3470 m, 2928 s, 2868 s, 1600 w, 1466 m, 1444 w, 1376 m, 1188 w, 1038 m, 978 w cm^{-1};^1H and ^{13}C NMR, see Table 1; FDMS *m/z* 428 (M^+ **11b**) and 414 (M^+ **11a**); EIMS (70 eV) *m/z* 428 (14, M^+ **11b**), 414 (49, M^+ **11a**), 410 (51), 396 (100), 381 (84), 274 (72), 259 (83), 149 (66), 141 (93), 95 (99), 69 (88); HREIMS *m/z* 428.3652 (calcd for $C_{29}H_{48}O_2$, 428.3654) and *m/z* 414.3496 (calcd for $C_{28}H_{46}O_2$, 414.3498).

3β-Hydroxy-28,29-bis-norcycloarten-6-one (12a) (50%) and 3β-Hydroxy-24-methylene-28,29-bis-norcycloartan-6-one (12b) (50%): IR (CCl_4) ν_{max} 3618 w, 2954 s, 2870 s, 1702 s, 1456 m, 1448 m, 1376 m, 1364 w, 1064 m, 982 w cm^{-1}; ^1H and ^{13}C NMR, see Table 1; FDMS *m/z* 426 (M^+ **12b**) and 412 (M^+ **12a**); EIMS (70 eV) *m/z* 426 (18, M^+ **12b**), 412 (29, M^+ **12a**), 259 (14), 149 (100), 134 (13), 121 (19), 109 (22), 95 (34), 69 (51); HREIMS *m/z* 426.3500 (calcd for $C_{29}H_{46}O_2$, 426.3498) and *m/z* 412.3340 (calcd for $C_{28}H_{44}O_2$, 412.3341).

28,29-*bis*-Norcycloarten-3β,4α,6α-triol (13a) (70%) and 24-Methylene-28,29-*bis*-norcycloartan-3β,4α,6α-triol (13b) (30%). IR ($CHCl_3$) ν_{max} 3590 m, 3472 m, 2940 s, 2870 s, 1602 w, 1468 m, 1448 m, 1376 m, 1320 m, 1142 m, 1112 m, 1054 s, 984 m cm^{-1};^1H and ^{13}C NMR, see Table 1; FDMS *m/z* 444 (M^+ **13b**) and 430 (M^+ **13a**); EIMS (70 eV) *m/z* 444 (18, M^+ **13b**), 430 (25, M^+ **13a**), 412 (16), 396 (13), 301 (13), 274 (27), 259 (20), 163 (74), 149 (65), 139 (72), 95 (95), 81 (59), 69 (100); HREIMS *m/z* 444.3607 (calcd for $C_{29}H_{48}O_3$, 444.3604) and *m/z* 430.3448 (calcd for $C_{28}H_{46}O_3$, 430.3447).

Acetylation of 13a+b. Compound **13a+b** (10 mg) was acetylated with Ac_2O in pyridine (room temperature, overnight) to give after usual workup and TLC purification 8 mg of **14a+b**; for ^1H and ^{13}C NMR, see Table 1.

(−)-Pannellin [Methyl 6,7,8,8a-Tetrahydro-8,8a-dihydroxy-9-methoxy-5a-(4-methoxyphenyl)-6-phenyl-5aH-cyclopenta[4,5]furo[2,3-*f*]-1,3-benzodioxole-7-carboxylate] (15): mp 102−104 °C; $[\alpha]^{20}_D$ − 50° (*c* 0.3, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 298 (3.73), 285sh (3.64), 228sh (4.11) nm; IR (CCl_4) ν_{max} 3648 w, 3582 w, 3543 w, 2952 m, 2926 s, 2854 m, 1754 m, 1732 m, 1638 w, 1620 w, 1514 m, 1488 m, 1454 s, 1440 m, 1378 w, 1312 w, 1298 w, 1252 s, 1206 m, 1182 m, 1164 s, 1130 m, 1118 s, 1068 m, 1048 m, 1032 w, 984 w, 948 w, 696 w cm^{-1}; ^1H NMR, see Table 2; ^{13}C NMR ($CDCl_3$) δ 170.7 (s, CO), 158.8 (s, C-4′), 154.2 (s, C-4a), 152.3 (s, C-6), 139.4 (s, C-8), 136.9 (s, C-1″), 130.2 (s, C-7), 128.9 (d, C-2′/6′), 127.8 (d, C-2″/6″), 127.7 (d, C-3″/5″), 126.6 (d, C-4″), 126.4 (s, C-1′), 112.8 (d, C-3′/5′), 110.2 (s, C-8a), 101.7 (s, C-3a), 101.3 (t, O−CH_2−O), 94.2 (s, C-8b), 88.5 (d, C-5), 79.5 (d, C-1), 60.0 (q, OCH_3-8), 55.09 (d, C-3), 55.07 (q, OCH_3-4′), 52.0 (q, ester CH_3), 50.4 (d, C-2); FDMS *m/z* 506 (M^+); EIMS (70 eV) *m/z* 506 (13, M^+), 342 (12), 328 (12), 314 (53, M^+ − $CH_2OH-CHCOOCH_3-CH_2C_6H_5$), 257 (15), 194 (32), 143 (38), 95 (36), 83 (68), 71 (64), 57 (100); HREIMS *m/z* 506.1581 (calcd for $C_{28}H_{26}O_9$, 506.1577).

(−)-Pannellin 1-*O*-acetate [Methyl 6,7,8,8a-Tetrahydro-8-acetyloxy-8a-hydroxy-9-methoxy-5a-(4-methoxyphenyl)-6-phenyl-5aH-cyclopenta[4,5]furo[2,3-*f*]-1,3-benzodioxole-7-carboxylate] (16): $[\alpha]^{20}_D$ −65° (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 298 (3.71), 285 sh (3.63), 228sh (4.08) nm; IR (CCl_4) ν_{max} 3575 w, 2952 m, 2929 m, 2855 w, 1754 s, 1641 m, 1616 m, 1513 m, 1498 m, 1453 s, 1441 m, 1371 m, 1312 w, 1252 s, 1229 s, 1180 m, 1164 m, 1132 m, 1118 m, 1098 w, 1069 m, 1045 m, 981 w, 948 w, 697m cm^{-1}; ^1H NMR, see Table 2; FDMS *m*/*z* 548 (M^+); EIMS (70 eV) *m*/*z* 548 (56, M^+), 488 (45, $M^+ - CH_3COOH$), 470 (32), 456 (16), 428 (15), 327 (27), 314 (100, $M^+ - CH_2OAc{-}CHCOOCH_3{-}CH_2C_6H_5$), 299 (44), 195 (43), 135 (55), 57 (50); HREIMS *m*/*z* 548.1685 (calcd for $C_{30}H_{28}O_{10}$, 548.1683).

(−)-3′-Methoxypannellin [Methyl 6,7,8,8a-Tetrahydro-8,8a-dihydroxy-9-methoxy-5a-(3,4-dimethoxyphenyl)-6-phenyl-5aH-cyclopenta[4,5]furo[2,3-f]-1,3-benzodioxole-7-carboxylate] (17): $[\alpha]^{20}_D$ −45° (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 298 sh (3.67), 285 (3.75), 228 sh (3.74) nm; IR (CCl_4) ν_{max} 3647 w, 3582 w, 3543 w, 2954 s, 2926 s, 2854 m, 1754 m, 1732 m, 1639 w, 1621 w, 1518 m, 1489 m, 1455 s, 1441 m, 1378 w, 1315 w, 1260 s, 1238 m, 1202 w, 1165 s, 1126 s, 1060 m, 1032 m, 948 w, 696 w cm^{-1};^1H NMR, see Table 2; FDMS *m*/*z* 536 (M^+); EIMS (70 eV) *m*/*z* 536 (25, M^+), 357 (10), 344 (100, $M^+ - CH_2OH{-}CHCOOCH_3{-}CH_2C_6H_5$), 329 (20), 195 (27), 165 (36), 131 (20), 97 (22), 85 (31), 71 (50), 57 (97); HREIMS *m*/*z* 536.1683 (calcd for for $C_{30}H_{28}O_{10}$, 536.1683).

Aglalactone [4-Methoxy-3-(*p*-methoxyphenyl)-5,6-methylenedioxy-2,3-dihydrobenzofuran-2-one] (18): $[\alpha]^{20}_D$ 0 ± 2° (*c* 0.1, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 304 (3.24), 268 (3.56), 235 (4.06) nm; IR (CCl_4) ν_{max} 3003 w, 2956 w, 2928 m, 2856 w, 1775 s, 1758 m, 1630 m, 1608 m, 1514 s, 1492 s, 1452 m, 1414 w, 1383 w, 1325 m, 1248 s, 1175 w, 1112 w, 1106 m, 1088 w, 1060 m, 1039 w, 1026 m, 1007 w, 989 w, 949 w, 881 w, 837 w cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17 (d, 2H, J = 8.7 Hz, H-2′ and H-6′), 6.88 (d, 2H, J = 8.7 Hz, H-3′, -5′), 6.31 (d, 1H, J = 0.5 Hz, H-7), 6.11 (br s, 1H, H-3), 6.05 and 6.03 (2 × d, 2H, J = 1.1 Hz, OCH_2O), 4.23 (s, 3H, OCH_3-4), 3.80 (s, 1H, OCH_3-4′); ^{13}C NMR ($CDCl_3$) δ 167.9 (s, CO), 160.3 (s, C-1′), 155.6 (s, C-7a), 148.0 (s, 6-H), 141.6 (s, C-4), 136.0 (s, C-1′), 128.6 (s, C-5), 128.5 (d, C-2′and C-6′), 114.3 (d, C-3′and C-5′), 110.3 (s, C-3a), 102.3 (t, OCH_2O), 96.9 (d, C-7), 81.0 (d, C-3), 60.6 (q, OCH_3-8), 55.3 (q, OCH_3-4′); FDMS *m*/*z* 314 (100, M^+); EIMS (70 eV) *m*/*z* 314 (67, M^+), 284 (23), 179 (100, $M^+ - CO - C_6H_4OCH_3$), 149 (30), 134 (23), 125 (12), 111 (17), 97 (23), 83 (25), 71 (29), 57 (47); HREIMS *m*/*z* 314.0795 (calcd for $C_{17}H_{14}O_6$, 314.0790).

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