Phytochemistry, Vol. 31, No. 12, pp. 4263–4274, 1992
Printed in Great Britain.

0031-9422/92 $5.00+0.00

CYCLOARTANES AND OTHER TERPENOIDS AND PHENYLPROPANOIDS FROM *MONOCYCLANTHUS VIGNEI**

HANS ACHENBACH and DIETER FREY

Institute of Pharmacy and Food Chemistry, Department of Pharmaceutical Chemistry, University of Erlangen, 8520 Erlangen, Germany

(*Received* 14 *April* 1992)

Key Word Index—*Monocyclanthus vignei*; Annonaceae; stem bark; cycloartanes; sterols; sesquiterpenes; geranic acid; phenylpropanoids.

Abstract—From the petrol extract of the stem bark of *Monocyclanthus vignei* 30 terpenoids and two phenylpropanoids have been isolated and their structures established, among them 17 new cycloartane-type compounds. Geranic acid and β-caryophyllene were found to be the major constituents.

INTRODUCTION

In the course of our phytochemical studies on tropical plants [1] we studied the constituents of *Monocyclanthus vignei* Keay. This plant of the Annonaceae family grows in West Africa as a small tree and represents the only species of its genus [2]. In a recent publication, we reported our investigation of the methanolic extract from the stem bark of *M. vignei*, which yielded 14 alkaloidal compounds, mainly of the aporphinoid and phenanthrene type [3]. The present work describes our study of the less polar constituents, which were contained in the petrol extract. Some of these results have already been published in a short preliminary note elsewhere [4].

RESULTS

Air-dried stem bark was extracted with petrol. Repeated column chromatography on silica gel and on organic gels resulted in the isolation of most of the compounds summarized in Table 1. However, some fractions needed special separation procedures. Thus, for the final purification of **2**, **3**, **10a/10b**, **14**, **17a/17b**, **18**, and **19** HPLC was used, **21** and **23** were separated by preparative GC, and the isolation of **25–27** was achieved by column chromatography on $AgNO_3$-coated silica gel.

The structures were established mainly by spectroscopic studies, sometimes in combination with chemical derivatizations or interconversions and, as far as possible, by comparison with authentic substances.

To establish a basis for the structure determinations of the cycloartanes, compound **1** was extensively studied by ^1H and ^{13}C NMR techniques. Using homo- and heteronuclear COSY the assignment of all signals was proven (Tables 2 and 3).

Our ^{13}C data differ partly from those reported for cycloartanone (**31**) [23], but they are in good agreement with the ^{13}C NMR resonances recently published for cycloartenol [24]. NOE studies corroborated our findings (Fig. 1) and in addition proved the relative configuration.

The absolute configuration of **1** was determined by its chemical conversion to cycloartanone [23, 25] via the epimeric mixture of the ketal-alcohols **32** according to Scheme 1.

In compound **2**, the ^1H NMR signal of H-3 appeared as a complex multiplet at δ3.27, which after acetylation was revealed as a double doublet with a *trans*-diaxial coupling constant ($J_1=11$, $J_2=5$ Hz) indicating a OH-3β group. In compound **3**, the resonance of H-3 was observed as a broad singlet at typically lower field ($\Delta\delta=0.19$ ppm) due to the stronger deshielding by the axial OH-3α [26, 27]. Consequently, compounds **2** and **3** were oxidized with pyridine chlorochromate (PCC). From both substances **1** was obtained as the only product, thereby establishing also the identical absolute configuration of the basic skeleton.

Compounds **4–15** differed from **1–3** by structural changes in the side chain at C-17 only. Thus the NMR spectra of both **4** and **5** indicated the presence of an aldehyde instead of the 21-methyl group [28] and a methylene instead of the 23-ketone. On oxidation, compound **5** was converted to **4**. NOE studies with **4** and a negative Cotton effect of **4** at 290 nm established the absolute configuration [29].

Structure **6** was determined from the spectra of the isolated compound and its acetylation product. The absolute configuration came from its oxidation with PCC, which yielded **4** as the only product.

Compound **7** was revealed as the corresponding 21-carboxylic acid and, consequently, the ^{13}C NMR signals of C-17 and C-20 to C-27 of **7** were found to be in complete agreement with those published for trametenolic acid [28]. Treatment of **7** with diazomethane gave the methyl ester, which on reduction with lithium aluminium hydride yielded **6**.

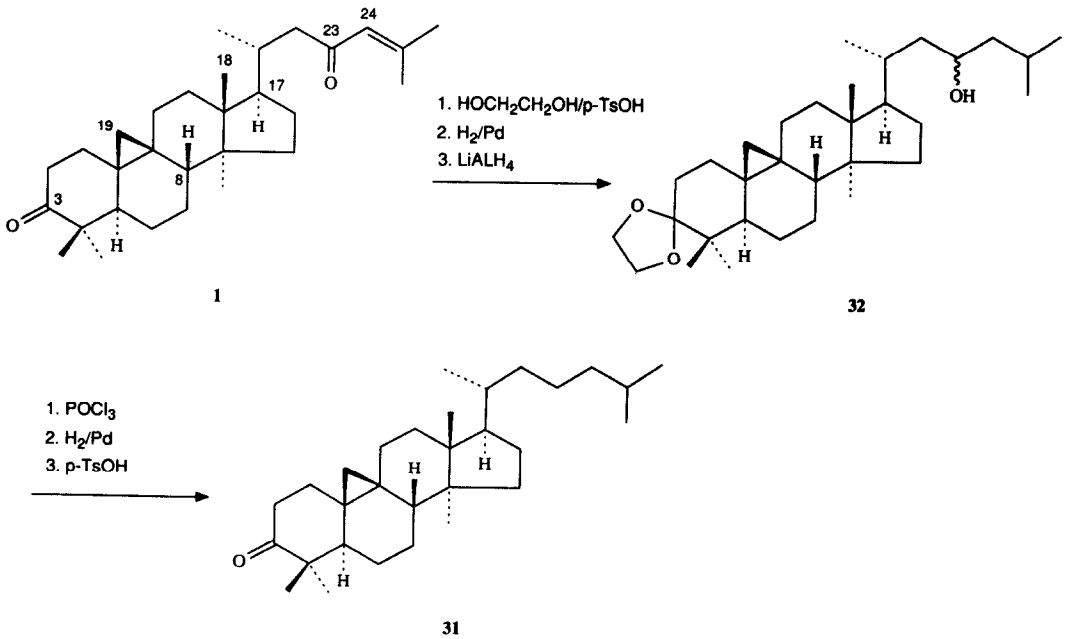
Compound **8** from its ^1H and ^{13}C spectra belongs to the 3β-hydroxycycloartane series. But in its NMR spectra various signals, and particularly those of C-20 to

*Part 54 in the series 'Constituents of Tropical Medicinal Plants'. For Part 53 see ref. [1].

Table 1. Compounds isolated from the petrol extract of the stem bark of *Monocyclanthus vignei*

Classification	Compound	Content [%]*	Refs
Terpenoids			
Triterpenes	5α-Cycloart-24-ene-3,23-dione (**1**)	0.25	
	3β-Hydroxy-5α-cycloart-24-en-23-one (**2**)	0.21	
	3α-Hydroxy-5α-cycloart-24-en-23-one (**3**)	0.07	
	3-Oxo-5α-cycloart-24-en-21-al (**4**)	0.04	
	3β-Hydroxy-5α-cycloart-24-en-21-al (**5**)	0.07	
	5α-Cycloart-24-ene-3β,21-diol (**6**)	0.50	
	3β-Hydroxy-5α-cycloart-24-en-21-oic acid (**7**)	0.03	
	(21*RS*,23*R*)-21,23-Epoxy-5α-cycloart-24-ene-3β,21-diol (**8**)	0.11	
	(23*R*)-5α-Cycloart-24-ene-3β,21,23-triol (**9**)	0.07	
	(23*RS*)-21,23-Epoxy-5α-cycloart-24-en-3-one (**10a/10b**)	0.25	
	(23*RS*)-21,23-Epoxy-5α-cycloart-24-en-3β-ol (**11a/11b**)	0.15	
	(23*S*)-21,23-Epoxy-5α-cycloart-24-en-3α-ol (**12**)	0.04	
	(21*R*,24*R*)-21,24-Cyclo-5α-cycloartane-3β,21,25-triol (**13**)	0.03	
	(21*R*,24*R*)-21,25-Dihydroxy-21,24-cyclo-5α-cycloartan-3-one (**14**)	0.03	
	(20*R*)-3β-Hydroxy-24,25,26,27-tetranor-5α-cycloartan-23,21-olide (**15**)	0.05	
	Eupha-8,24-dien-3β-ol (**16**)	0.01	[5, 6]
Sterols	7-Oxostigmast-5-en-3β-yl oleate (**17a**)	0.03	
	7-Oxostigmast-5-en-3β-yl palmitate (**17b**)	0.01	
	Sitosterol (**18**)	0.05	[7, 8]
	Stigmasterol (**19**)	0.03	[9, 10]
Sesquiterpenes	T-Cadinol (**20**)	0.04	[11, 12]
	β-Caryophyllene (**21**)	2.4	[13]
	Caryophyllene oxide (**22**)	0.36	[13]
	α-Copaene (**23**)	0.6	[14]
	α-Cyperone (**24**)	0.01	[15]
	Elemol (**25**)	0.02	[16, 17]
	α-Eudesmol (**26**)	0.01	[18]
	β-Eudesmol (**27**)	0.45	[18]
Monoterpenes	Geranic acid (**28**)	6.7	[19, 20]
Phenylpropanoids	Elemicin (**29**)	0.05	[21]
	(*E*)-Isoelemicin (**30**)	0.07	[22]

*Dry wt of extract = 100%.



Scheme 1. Chemical conversion of **1** to cycloartanone (**31**).

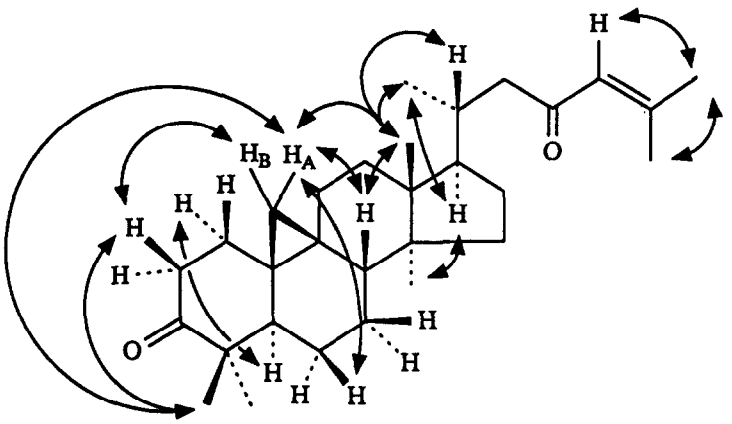
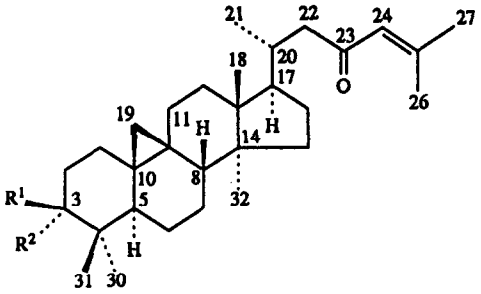
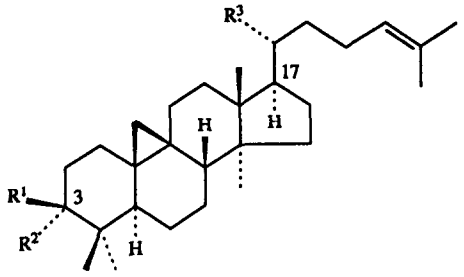


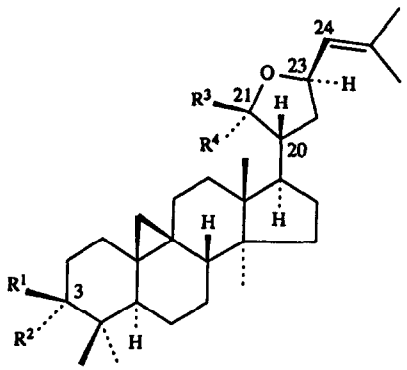
Fig. 1. Nuclear Overhauser effects observed for compound 1.

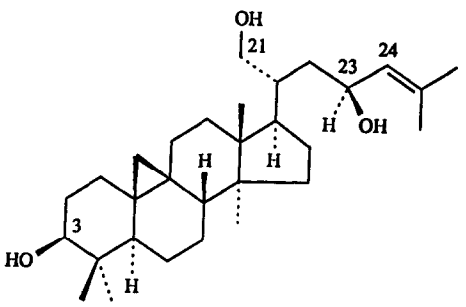




1 R^1,R^2 = O
2 R^1 = OH, R^2 = H
3 R^1 = H, R^2 = OH

4 R^1,R^2 = O, R^3 = CHO
5 R^1 = OH, R^2 = H, R^3 = CHO
6 R^1 = OH, R^2 = H, R^3 = CH_2OH
7 R^1 = OH, R^2 = H, R^3 = COOH

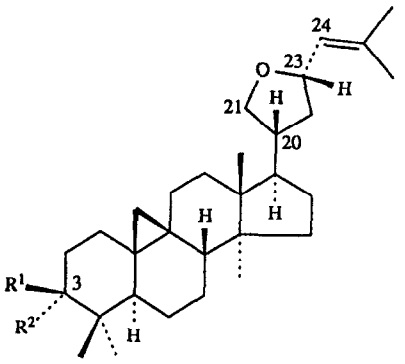




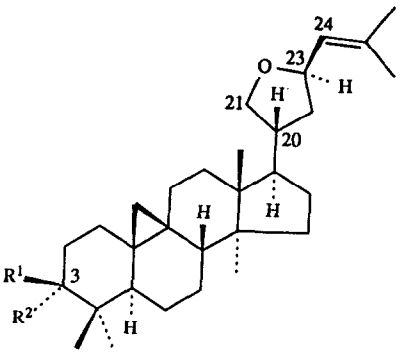
8 $\begin{cases} R^1 = R^3 = OH, R^2 = R^4 = H \\ R^1 = R^4 = OH, R^2 = R^3 = H \end{cases}$

9

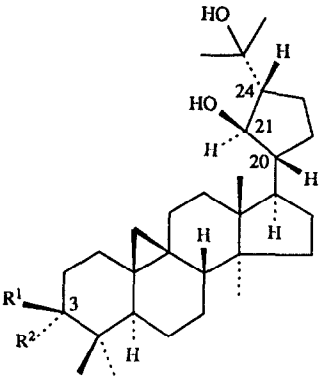
33 $R^1 = R^4 = OCOCH_3$, $R^2 = R^3 = H$
34 $R^1 = R^3 = OCOCH_3$, $R^2 = R^4 = H$
35 R^1,R^2 = O, R^3,R^4 = O



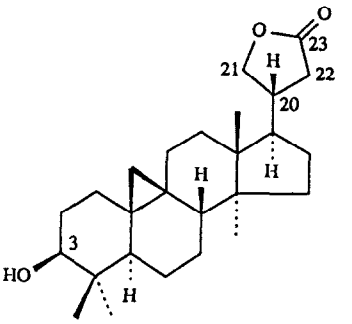
10a R^1,R^2 = O
11a R^1 = OH, R^2 = H
12 R^1 = H, R^2 = OH



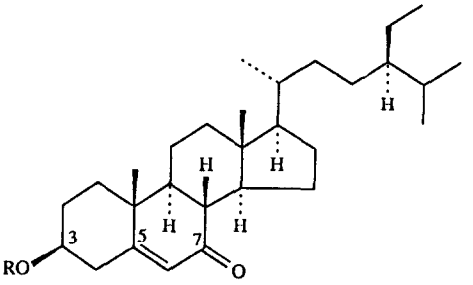
10b R^1,R^2 = O
11b R^1 = OH, R^2 = H



13 R^1 = OH, R^2 = H
14 R^1,R^2 = O



15



17a R = $H_3C-(CH_2)_7-CH\overset{Z}{=}CH-(CH_2)_7-CO-$
17b R = $H_3C-(CH_2)_{14}-CO-$

Table 2. ^{1}H NMR spectral data of compound **1**

H	δ [ppm]	J [Hz]
1α	1.85 *dddd*	14, 14, 4.5, 1†
1β	1.54 *ddd*	14, 6.5, 2.5
2α	2.30 *ddd*	14, 4.5, 2.5
2β	2.71 *ddd*	14, 14, 6.5
5	1.71 *dd*	12.5, 4.5
6α	1.56 *dddd*	12.5, 4.5, 4.5, 2.5
6β	0.95 *dddd*	12.5, 12.5, 12.5, 2.5
7α	1.14 *dddd*	12.5, 12.5, 12.5, 2.5
7β	1.38 *dddd*	12.5, 4.5, 4.5, 2.5
8	1.60 *dd*	12.5, 4.5
11_A	~2.1*	
11_B	~1.2*	
12_A	~1.7*	
12_B	~1.7*	
15_A	~1.3*	
15_B	~1.3*	
16_A	~1.9*	
16_B	~1.3*	
17	~1.7*	
Me-18	1.04 *s*	
19_A	0.79 *br d*	4.2
19_B	0.58 *d*	4.2
20	2.02 *m*	
Me-21	0.89 *d*	6.5
22_A	2.51 *dd*	15, 2.5
22_B	2.11 *dd*	15, 10
24	6.06 *qq*	1.2, 1.2
Me-26	2.15 *d*	1.2
Me-27	1.89 *d*	1.2
Me-30	1.04 *s*	
Me-31	1.10 *s*	
Me-32	0.91 *s*	

*Overlapped multiplet.
†*W*-Coupling to H-19_A.

C-24, appeared twice and, therefore, suggested a mixture of epimers. Consequently, compound **8** was (i) acetylated and (ii) oxidized with PCC. Acetylation yielded a mixture of the epimeric diacetyl derivatives **33** and **34**, which could be separated by HPLC. The ^{1}H and ^{13}C NMR spectra, including NOE studies, determined their structures. In **34**, the resonance of H-20 appears at significantly lower field than in **33** ($\Delta\delta$H-20 = 0.14 ppm), due to the influence of the neighbourhood of the carbonyl group. Further arguments for the stereochemistry at C-20 and C-21 come from the fact, that in the ^{13}C NMR spectrum vicinal substituents at five-membered rings, if *trans*-positioned, always cause a low-field shift of the substituted carbon atoms in comparison to the *cis*-isomer. In addition, the signals of the α-carbon atoms of the substituents (in our case: C-17) experience a typical low-field shift only in the *trans*-isomer [30]. The stereochemistry at C-23 was determined from the cycloartan-3-one derivative (**35**), which was produced by oxidation of **8** and contains a γ-lactone moiety as part of the side chain. ^{1}H COSY corroborated its structure and NOE measurements established its relative configuration. The absolute configuration came from CD studies: whereas the negative Cotton effect at 290 nm indicates the 'normal' absolute configuration of the cycloartan-3-one ring system [29], the observed positive Cotton effect at 219 nm in connection with corresponding conformational considerations is typical for the 4*R*-configuration of γ-lactones carrying a vinyl substituent at C-4 [31].

The NMR spectra of **9** closely resembled those of **6** and indicated an additional hydroxyl group at C-23. Consequently, hemi-acetal **8** was reduced with $LiAlH_4$: the identity of the product with **9** corroborated the structure of **9** and also established its absolute configuration.

According to the ^{1}H NMR spectrum, **10** consisted of an (inseparable) mixture of the major component **10a** and a minor isomer **10b**. The NMR spectra indicated a cycloartan-3-one ring skeleton and with regard to the substituent at C-17 they showed close similarities with **9**. However, two signals for C–O carbon atoms (δ75.2 and 71.3) together with the absence of any hydroxyl group suggested a cyclic ether moiety within the side chain and further NMR studies established a 2,4-disubstituted tetrahydrofuran. The determination of the stereochemistry of the tetrahydrofurans is possible from the ^{13}C spectra, but this needs the data of both stereoisomers [30]. Therefore, it was established to be *cis* (=23*S*) by comparison of the ^{13}C NMR spectral data of **10a** with those of **11a** and **b** (see below) and by the chemical conversion of **11** to **10**. NOE studies and the negative Cotton effect at 293 nm determined the absolute configuration. The second set of ^{1}H signals, particularly those for H-21, H-23 and H-24, in the ^{1}H NMR spectrum of **10** with a 9:1 ratio of the integral had to be attributed to the 23*R*-epimer **10b** with a *trans*-disubstituted tetrahydrofuran as the minor component. The concentration was too low to determine the ^{13}C NMR spectral data of **10b**. All chromatographic attempts (HPLC, GC) to separate the diastereomers failed.

The structure of **11** was established as the 3β-cycloartanol analogue of **10**; doubled NMR signals here also indicated the presence of a mixture of the 23-epimers **11a** and **b** in a 4:1 ratio. However, since in this case the ^{13}C NMR data of both epimers were available from the spectrum of the chromatographically inseparable mixture, it was possible to establish the relative configuration at the 2,4-disubstituted tetrahydrofuran ring system: the resonances of both substituted carbon atoms (C-20 and C-23) as well as the carbon inbetween (C-22) appear in the major component **11a** shifted to lower fields as compared with the minor isomer **11b** and the reverse effect was observed for the remaining atom of the tetrahydrofuran (C-21). This clearly indicates the 20,23-*cis*-configuration (=23*S*) for **11a** and the *trans*-configuration in **11b** [30].

Compound **12** by its NMR spectra was revealed as the 3α-epimer of **11**. Contrary to **10a/b** and **11a/b** it was obtained by the standard chromatographic procedures as a pure compound. Oxidation converted **11** and **12** to **10** and thereby established the absolute configurations.

The spectra showed that **13** and **14** also belong to the cycloartanes and differ from each other by the oxygen function at C-3 only. The NMR signals of the 21-methyl group were missing, and ^{1}H resonances of two methyl groups in agreement with the ^{13}C data appeared as singlets with low-field shifts typical for a 2-hydroxyisopropyl group [32]. ^{1}H and ^{13}C NMR studies with **13** (^{1}H/^{1}H and ^{1}H/^{13}C COSY, DEPT) revealed that it belongs to the cycloartan-3β-ol series and that carbon atoms C-20 to C-24 form a 2,5-disubstituted cyclopentanol. The relative configuration of the substituents at

the cyclopentanol was established from the coupling constants of the carbinol proton H-21 (*dd*, $J_1 = 8.5$, $J_2 = 7$ Hz): the observed large coupling constants with both vicinal protons demand the *trans*-orientation of the substituents [33]. Significant nuclear Overhauser effects between H-21 and H-17 as well as H-21 and one of the protons at C-12 corroborated, among others, the β-configuration of the cyclopentanol moiety at C-17.

The structure of **14** was corroborated by reduction of its 3-keto function with $LiAlH_4$, which yielded **13** as the major product [26]. The negative Cotton effect at 293 nm in **14** established the absolute configurations of **13** and **14**.

From the NMR spectra, **15** also belongs to the 3β-cycloartanol series; but with only 26 carbon atoms the C-17 side chain has to be shortened, and as the spectra showed it cannot contain any methyl groups. A typical band in the IR ($\nu_{C=O}$ 1774 cm^{-1}) and corresponding NMR signals suggested a γ-lactone as the substituent at C-17. This structural element was corroborated by $^1H/^1H$ COSY and by comparison of the NMR data with those of dihydrodigitoxigenin [34]. The relative configuration between C-17 and C-20 came from comparison of the ^{13}C NMR data with those of **10**–**12**. A positive Cotton effect at 217 nm gives evidence for the *R*-configuration at C-20 [35]. The absolute configuration of the basic cycloartane ring system is corroborated by oxidation of **15** with PCC to the corresponding 3-keto compound, which exhibited a negative Cotton effect at 294 nm.

Among the sterols, the two esters **17a** and **b** came off the HPLC columns as a mixture; attempts to achieve further separation failed. Therefore, the mixture was subjected to methanolysis to yield 3β-hydroxystigmast-5-en-7-one [36, 37] and two fatty acid methyl esters, which were analysed by GC-MS to be esters of oleic acid (75%) and palmitic acid (25%), respectively.

*Very recently **1** has also been described from a Fijian *Gardenia* species [46].

DISCUSSION

The major non-polar constituents of the stem bark of *M. vignei* are geranic acid and β-caryophyllene. Whereas the various isolated sesquiterpenes are comparatively ubiquitous natural products, among the triterpenes eupha-8,24-dien-3β-ol (**16**) [5, 6] has been detected within the Annonaceae family for the first time and the 17 cycloartanes described above all represent new natural products.*

Besides the functional group at C-3, these cycloartanes mutually differ by the structures of their C-17 side chains. Corresponding structures for the substituents at C-17 only have already been reported occasionally in other groups of triterpenes or steroids, e.g. the hemiacetal-type side chain of **8** as in the tirucullane-type triterpene flindissol [38].

Only very recently, the 1,4-dihydroxy-6-methyl-hept-5-en-2-yl substituent at C-17 of a sterol-type cyclic system as in **9** has also been described, but without determination

Table 3. ^{13}C NMR spectral data of compounds **1**–**15** (in $CDCl_3$)

C	1	2	3	4	5	6	7
1	33.3 (CH_2)	32.1	27.5[a]	33.3	31.9	32.1	31.9
2	37.4 (CH_2)	30.5	28.7	37.4	30.4	30.5	30.3
3	216.4 (C)	78.9	76.7	216.1	78.8	78.9	78.8
4	50.1 (C)	40.6	39.6	50.2	40.5	40.6	40.4
5	48.3 (CH)	47.3	41.1	48.3	47.0	47.3	47.4
6	21.4 (CH_2)	21.2	21.3	21.3	21.0	21.1	20.9
7	25.8 (CH_2)	26.0	25.8	25.8[b]	25.9	26.0	25.9[a]
8	47.8 (CH)	47.9	48.0	47.5	47.5	47.8	47.6
9	20.9 (C)	20.1	19.9	21.0[a]	20.0	20.2	19.9
10	25.9 (C)	26.3	26.3	25.9[b]	26.3	26.5[a]	25.9[a]
11	26.6 (CH_2)	26.6	26.6	26.5	26.5	26.7[a]	26.3[a]
12	32.6 (CH_2)	33.0	32.9	31.4	31.5	32.3	32.6
13	45.4 (C)	45.6	45.5	45.3	45.3	45.5	45.1
14	48.8 (C)	49.1	49.1	48.6	48.7	49.0	48.6
15	35.4 (CH_2)	35.6	35.5	35.2	35.2	35.6	34.9
16	28.3 (CH_2)	28.4	28.4	29.4[c]	29.4	27.5	30.0
17	52.4 (CH)	52.7	52.6	47.5	47.5	46.6	49.1
18	18.1 (CH_3)	18.1	18.0	18.9	18.8	18.1	19.2
19	29.5 (CH_2)	29.8	29.8	29.4	29.8	29.8	29.7
20	33.3 (CH)	33.5	33.5	55.4	55.4	42.7	46.9
21	19.2[a] (CH_3)	19.5[a]	19.4[b]	205.7	205.6	63.1	181.4
22	51.7 (CH_2)	51.8	51.8	26.9[c]	26.9	30.1	27.2
23	201.4 (C)	201.4	201.5	26.3[b]	25.9	25.3[b]	26.2[a]
24	124.3 (CH)	124.6	124.5	123.6	123.6	125.1	123.6
25	154.6 (C)	154.1	154.3	132.5	132.4	131.3	132.2
26	20.6[b] (CH_3)	20.6	20.6	17.7	17.7	17.7	17.6
27	27.6 (CH_3)	27.5	27.6[a]	25.6[b]	25.6[a]	25.5[b]	25.7
30	22.1 (CH_3)	25.5	25.6	22.2	25.5[a]	25.5[b]	25.4
31	20.7[b] (CH_3)	14.0	21.1	20.7[a]	13.9	14.0	14.0
32	19.3[a] (CH_3)	19.4[a]	19.3[b]	19.2	19.2	19.5	19.3

Table 3. (*Continued*)

C	8*†	9†	10a	11a/11b*	12	13	14	15
1	31.8[a]	31.7[a]	33.3	31.9	27.5	32.0 (CH_2)	33.4	31.9 (CH_2)
2	30.4	29.3[b]	37.3	30.4	28.5	30.5 (CH_2)	37.5	30.3 (CH_2)
3	79.0	78.7	216.1	78.8	76.6	78.9 (CH)	216.4	78.7 (CH)
4	40.9	40.2	50.1	40.4	39.5	40.5 (C)	50.2	40.5 (C)
5	47.6	47.0	48.3	47.0	40.9	47.1 (CH)	48.4	46.9 (CH)
6	21.3	20.7	21.3[a]	21.0	21.2[a]	21.0 (CH_2)	21.3[a]	20.9 (CH_2)
7	26.3	25.6	25.8[b]	26.0[a]	25.9[b]	26.0 (CH_2)	25.8	25.9 (CH_2)
8	48.0	47.6	47.6	47.8	47.9	47.7 (CH)	47.6	47.7 (CH)
9	20.6, 20.5‡	19.8	21.1[a]	20.1	19.8[a]	20.2 (C)	21.4[a]	19.8 (C)
10	26.8, 26.9‡	26.1	25.7[b]	25.8[a]	25.8[b]	26.3 (C)	26.3	26.4 (C)
11	27.0	26.2	26.6	26.5	26.7	26.5 (CH_2)	26.5	26.1 (CH_2)
12	32.4[a]	32.0[a]	31.3	31.3	31.2	31.0 (CH_2)	30.7	31.5 (CH_2)
13	45.6, 45.9‡	45.1	45.6	45.5	45.4	45.5 (C)	45.5	45.5 (C)
14	48.9	48.7	48.3	48.4	48.4	48.6 (C)	48.4	48.4 (C)
15	35.7, 35.8‡	35.2	35.8	35.8	35.7	35.5 (CH_2)	35.5	35.6 (CH_2)
16	27.8, 28.0‡	27.3	27.9	27.9	27.9	26.5 (CH_2)	26.8	27.4 (CH_2)
17	49.9, 49.4‡	46.1	51.0	51.0, 50.8‡	50.9	50.7 (CH)	50.8	50.8 (CH)
18	19.5, 19.0‡	17.7	18.8	18.7	18.7	19.1 (CH_3)	19.0	18.9 (CH_3)
19	30.1	29.7[b]	29.6	29.9	29.9	29.9 (CH_2)	29.5	29.9 (CH_2)
20	46.5, 46.0‡	39.7[c]	40.4	40.5, 39.2‡	40.4	47.7 (CH)	47.6	39.2 (CH)
21	97.8, 101.7‡	63.7	71.3	71.4, 72.0‡	71.4	79.1 (CH)	79.1	72.5 (CH_2)
22	36.2, 36.7‡	39.4[c]	43.7	43.7, 42.5‡	43.7	27.4 (CH_2)	27.5	34.7 (CH_2)
23	73.6, 75.7‡	65.5	75.2	75.2, 74.4‡	75.2	24.6 (CH_2)	24.5	176.7 (C)
24	127.5, 128.3‡	128.3	126.4	126.4, 127.0‡	126.3	57.7 (CH)	57.6	—
25	134.8	132.8	135.4	135.5	135.7	73.4 (C)	73.6	—
26	18.0	17.4	18.1	18.1	18.1	24.5[a] (CH_3)	24.3[b]	—
27	25.7	24.9	26.3	26.3	26.1[b]	30.6[a] (CH_3)	30.7[b]	—
30	25.7	24.9	22.2	25.4	25.6	25.5 (CH_3)	22.2	25.4 (CH_3)
31	14.2	13.5	20.7	14.0	20.9[a]	14.0 (CH_3)	20.8	13.9 (CH_3)
32	19.6	19.0	19.2	19.3	19.2	19.4 (CH_3)	19.4	19.2 (CH_3)

[a–c]Assignments may be interchangeable in each vertical column.
*Mixture of epimers.
†Measured in $CDCl_3$–CD_3OD (1:1).
‡Signal of the minor epimer.
( )Result of DEPT measurements.

of the stereochemistry, in the fruit from a *Paramignya* species [39]. However, the cyclopentane-forming side chains of **13** and **14** represent unique structural elements among the terpenoids and **15** has to be regarded a new member of the small group of tetranortriterpenes.

The esters **17a** and **b** are also new compounds. From a phytochemical point of view it should be noticed that the free 3β-hydroxystigmast-5-en-7-one could not be detected in the plant extract.

The above results came from analysis of the stem bark. TLC comparison of an extract from the twigs and leaves of *M. vignei* with the extract from the stem bark did not show major differences of the constituents.

EXPERIMENTAL

General. Mps: uncorr. Analytical TLC was performed on precoated plates (Nano plates Sil-20 UV, Macherey–Nagel) using the systems: S-1 = petrol–Me_2CO (9:1), S-2 = petrol–Me_2CO (4:1), S-3 = petrol–Me_2CO (7:3), S-4 = petrol–EtOAc (1:1); detection: anisaldehyde [40] followed by heating. If not stated otherwise, $[\alpha]_D$ in $CHCl_3$; UV and CD were run in MeOH. IR in $CHCl_3$. MS were obtained at 70 eV. Unless key ions, ions are given with intensities > 20% and m/z > 100. If not otherwise stated, ^{1}H NMR were recorded at 400 MHz and ^{13}C NMR at 22.5 MHz in $CDCl_3$ with TMS as the int. standard.

Acetylation. The sample (5–20 mg) was dissolved in a 1:1-mixture of pyridine and Ac_2O (0.5–2 ml) and stirred for 12 hr at room temp. After removal of the reaction mixture by vacuum evapn the product was purified by CC or HPLC over silica gel.

Oxidation [41]. The sample (*ca* 2 mg) was rapidly added to a suspension of excess pyridinium chlorochromate in CH_2Cl_2 (2 ml) at room temp. After stirring for 1.5 hr, dry Et_2O (5 ml) was added and the liquid phase decanted from the ppt., which subsequently was extracted with Et_2O (3 × 5 ml). The combined organic solns were evapd and purified by CC over silica gel (petrol–Me_2CO, 19:1).

Reduction with $LiAlH_4$. The sample (*ca* 2 mg) was dissolved in dry Et_2O (2–5 ml) and excess $LiAlH_4$ added. After stirring for 30 min at room temp., Me_2CO (2 ml) was added and then the reaction mixture was filtered, evapd and the product purified by CC over silica gel.

Plant material. Stem bark of *Monocyclanthus vignei* Keay was collected in March 1985 at Ankasa Forest Reserve (Ghana) and identified by Mr A. A. Enti (Forestry Enterprises, Legon, Ghana). A voucher specimen (No. 8507) is deposited in our institute in Erlangen [3, 4].

Extraction and isolation. Ground stem bark (2 kg) was extracted at room temp. with petrol yielding 24 g residue, which was chromatographed on 500 g silica gel (Macherey–Nagel, No. 81538) using $CHCl_3$ and $CHCl_3$–MeOH (increasing concn of MeOH). Further sepn was achieved by subsequent and repeated CC using the following systems: (a) silica gel, petrol–Me_2CO, (b) silica gel, petrol–EtOAc, (c) silica gel, cyclohexane–EtOAc, (d) Fractogel PVA 500, MeOH–$CHCl_3$ (7:3), (e) Sephadex LH 20, MeOH–$CHCl_3$ (7:3). This yielded compounds **1**, **4–9**, **11–13**, **15–16**, **20**, **22**, **24** and **28–30**.

Isolation of **2**, **3**, more **5** and **8**, **10** and **14** was performed from corresponding CC-fractions by HPLC on silica gel (Nucleosil®) with (f) petrol–EtOH (99:1), (g) petrol–EtOH (49:1), (h) petrol–EtOH (24:1).

Isolation of **17–19** was achieved by HPLC on silica gel RP-18 (Lichrosorb®) using (i) MeOH, (j) MeOH–EtOH (3:2).

The CC-fraction containing a mixture of **21** and **23** was sepd by prep. GC.

Final separation of the CC-fractions containing **25–27** was performed by CC on silica gel precoated with $AgNO_3$ (15%) using petrol–Me_2CO or with $AgNO_3$ (10%) using cyclohexane–EtOAc.

5α-Cycloart-24-ene-3,23-dione (**1**). Crystals (61 mg). Mp 137–138° (from $CHCl_3$–MeOH, 1:1). TLC: R_f 0.40 (S-1), 0.55 (S-2); anisaldehyde reagent: brown-orange. $[\alpha]_D^{21}$ +6° (*c* 0.85). CD nm (Δε): 260 (+0.09), 298 (−0.61), 330 (−0.2, sh). UV λ_{max} nm (log ε): 237 (4.25). IR ν_{max} cm^{-1}: 1699, 1680, 1616. ^1H NMR: Table 2. ^{13}C NMR (100 MHz): Table 3. EIMS *m/z* (rel. int.): 438.3498 $[M]^+$ (calcd for $C_{30}H_{46}O_2$: 438.3498) (12), 340 (41), 325 (10), 313 (7), 175 (9), 147 (41), 125 (97), 121 (37), 98 (44), 83 (100).

3,3-Ethylenedioxy-5α-cycloart-24-en-23-one. Compound **1** (16 mg), *p*-toluenesulphonic acid (1 mg) and ethylene glycol (35 mg) were refluxed in C_6H_6 (25 ml) for 2 hr with azeotropic removal of H_2O. Work-up and purification by CC (basic Al_2O_3; petrol–Me_2CO, 99:1) yielded 3,3-ethylenedioxy-5α-cycloart-24-en-23-one (11 mg). Mp 90° (from Me_2CO). TLC: R_f 0.61 (S-2); anisaldehyde reagent: brown. $[\alpha]_D^{21}$ +7° (*c* 1.14). UV λ_{max} nm (log ε): 238 (4.27). IR ν_{max} cm^{-1}: 1681, 1616. ^1H NMR: δ 0.37 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.58 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.84 (3H, *s*, Me-31), 0.88 (3H, *d*, *J* = 6.5 Hz, Me-21), 0.88 (3H, *s*, Me-32), 0.97 (3H, *s*, Me-30), 1.02 (3H, *s*, Me-18), 1.88 (3H, *d*, *J* = 1.2 Hz, Me-27), 2.09 (1H, *dd*, J_1 = 15, J_2 = 10 Hz, H-22$_B$), 2.14 (3H, *d*, *J* = 1.2 Hz, Me-26), 2.51 (1H, *dd*, J_1 = 15, J_2 = 2.5 Hz, H-22$_A$), 3.91–4.00 (4H, *m*, O–CH_2–CH_2–O), 6.06 (1H, *m*, H-24). ^{13}C NMR: δ 18.1, 18.8 (C-18, C-30), 19.3, 19.4 (C-21, C-32), 19.8 (C-31), 20.6 (C-9), 20.6 (C-26), 21.2 (C-6), 25.9, 26.0 (C-7, C-10), 26.5 (C-11), 27.6 (C-27), 28.4 (C-16), 29.8 (C-19), 30.0 (C-2), 30.7 (C-1), 32.9 (C-12), 33.5 (C-20), 35.6 (C-15), 44.0 (C-4), 44.9 (C-5), 45.5 (C-13), 48.0 (C-8), 49.0 (C-14), 51.8 (C-22), 52.6 (C-17), 64.9, 65.0 (O–CH_2–CH_2–O), 113.5 (C-3), 124.5 (C-24), 154.2 (C-25), 201.5 (C-23). EIMS *m/z* (rel. int.): 482 $[M]^+$ (15), 383 (6), 99 (100), 83 (12).

3,3-Ethylenedioxy-5α-cycloartan-23-one. 3,3-Ethylenedioxy-5α-cycloart-24-en-23-one (11 mg) in MeOH (2 ml) was stirred in the presence of Pd/C 5% under H_2 for 2 hr. After filtration and evapn CC (silica gel; petrol–Me_2CO, 99:1) gave 3,3-ethylenedioxy-5α-cycloartan-23-one (10 mg). Mp 90–91° (from Me_2CO). TLC: R_f 0.64 (S-2); anisaldehyde reagent: brown. $[\alpha]_D^{21}$ +17° (*c* 0.72). IR ν_{max} cm^{-1}: 1703. ^1H NMR: δ 0.37 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.58 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.84 (3H, *s*, Me-31), 0.86 (3H, *d*, *J* = 6.5 Hz, Me-21), 0.88 (3H, *s*, Me-32), 0.90, 0.92 (each 3H, *d*, *J* = 6.5 Hz, Me-26, Me-27), 0.97 (3H, *s*, Me-30), 1.01 (3H, *s*, Me-18), 2.25 (2H, *d*, *J* = 6.5 Hz, H-24$_A$, H-24$_B$), 2.43 (1H, *dd*, J_1 = 15, J_2 = 2.5 Hz, H-22$_A$), 3.91–4.00 (4H, *m*, O–CH_2–CH_2–O). EIMS *m/z* (rel. int.): 484 $[M]^+$ (2), 469 (1), 441 (1), 398 (1), 384 (1), 302 (2), 298 (2), 99 (100), 87 (18), 57 (12).

(23R)- and (23S)-3,3-Ethylenedioxy-5α-cycloartan-23-ol (mixture of the 23-epimers) (**32**). 3,3-Ethylenedioxy-5α-cycloartan-23-one (10 mg) in dry Et_2O was treated with excess $LiAlH_4$ at room temp. for 0.5 hr. Work-up gave a product which by CC on silica gel (petrol–Me_2CO, 49:1) afforded **32**. Amorphous (9 mg). TLC: R_f 0.52 (S-2); anisaldehyde reagent: lilac. IR ν_{max} cm^{-1}: 3621. ^1H NMR: δ 0.37 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.57 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.84 (3H, *s*, Me-31), 0.88 (3H, *s*, Me-32), 0.91 (9H, *d*, *J* = 6.5 Hz, Me-21, Me-26, Me-27), 0.97 (3H, *s*, Me-30), 1.00 (3H, *s*, Me-18), 1.90 (1H, *m*), 2.02 (1H, *m*), 3.79 (1H, *m*, H-23), 3.91–4.00 (4H, *m*, O–CH_2–CH_2–O). EIMS *m/z* (rel. int.): 486 $[M]^+$ (8), 471 (2), 443 (3), 400 (4), 304 (3), 271 (2), 181 (4), 99 (100), 87 (14).

Cycloartanone (**31**). To a soln of **32** in pyridine $POCl_3$ (1 drop) was added at 0°. After stirring for 12 hr, the reaction mixture was poured slowly into ice/H_2O and extracted with $CHCl_3$. After removal of the $CHCl_3$ the product was hydrogenated in MeOH (2 ml) in the presence of Pd/C 5% as described above. Deketalization was achieved by *p*-TsOH in EtOH and subsequent purification by HPLC (silica gel RP-18; EtOH–H_2O, 19:1) yielded **31** (1.7 mg). Mp 107–109° (from Me_2CO) (ref. [25] mp 110°). TLC: R_f 0.56 (S-1); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +23° (*c* 0.11) (ref. [25] $[\alpha]_D$ +24° (*c* 2.9)). CD nm (Δε): 295 (−0.45) [29]. ^1H NMR, ^{13}C NMR, EIMS identical with an authentic sample.

3β-Hydroxy-5α-cycloart-24-en-23-one (**2**). Crystals (51 mg). Mp 130° (from Me_2CO). TLC: R_f 0.34 (S-2), 0.51 (S-3), 0.58 (S-4); anisaldehyde reagent: brown-orange. $[\alpha]_D^{21}$ +18° (*c* 0.9). UV λ_{max} nm (log ε): 238 (4.27). IR ν_{max} cm^{-1}: 3616, 1681, 1616. ^1H NMR: δ 0.34 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.56 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.79 (1H, *dddd*, $J_1 = J_2 = J_3$ = 12.5, J_4 = 2.5 Hz, H-6β), 0.81 (3H, *s*, Me-31), 0.88 (3H, *d*, *J* = 6.5 Hz, Me-21), 0,90 (3H, *s*, Me-32), 0.97 (3H, *s*, Me-30), 1.02 (3H, *s*, Me-18), 1.88 (3H, *d*, *J* = 1.2 Hz, Me-27), 2.10 (1H, *dd*, J_1 = 15, J_2 = 10 Hz, H-22$_B$), 2.14 (3H, *d*, *J* = 1.2 Hz, Me-26), 2.51 (1H, *dd*, J_1 = 15, J_2 = 2.5 Hz, H-22$_A$), 3.27 (1H, *m*, H-3α), 6.06 (1H, *m*, H-24). ^{13}C NMR: Table 3. EIMS *m/z* (rel. int.): 440.3654 $[M]^+$ (calcd for $C_{30}H_{48}O_2$: 440.3654) (10), 425 (5), 422 (10), 407 (10), 342 (6), 327 (5), 324 (6), 315 (10), 309 (7), 300 (10), 255 (8), 202 (18), 175 (15), 147 (38), 125 (60), 98 (17), 83 (100).

23-Oxo-5α-cycloart-24-en-3β-yl acetate. Acetylation of **2** (5 mg) gave its monoacetyl ester. Crystals (5 mg). Mp 143–145° (from Me_2CO). TLC: R_f 0.56 (S-2); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +30° (*c* 0.47). IR ν_{max} cm^{-1}: 1726, 1681, 1616. ^1H NMR: δ 0.34 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.59 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.85 (3H, *s*, Me-31), 0.88 (3H, *d*, *J* = 6.5 Hz, Me-21), 0.89 (3H, *s*, Me-30), 0.91 (3H, *s*, Me-32), 1.01 (3H, *s*, Me-18), 1.88 (3H, *d*, *J* = 1.2 Hz, Me-27), 2.05 (3H, *s*, OCOMe), 2.14 (3H, *d*, *J* = 1.2 Hz, Me-26), 2.51 (1H, *dd*, J_1 = 15, J_2 = 2.5 Hz, H-22$_A$), 4.57 (1H, *dd*, J_1 = 11, J_2 = 5 Hz, H-3α), 6.06 (1H, *m*, H-24). EIMS *m/z* (rel. int.): 482 $[M]^+$ (2), 422 (7), 407 (14), 384 (16), 379 (9), 324 (12), 147 (25), 125 (43), 121 (25), 83 (100), 55 (50), 43 (98).

Compound **1** *by oxidation of* **2**. Oxidation of **2** (2.2 mg) with pyridine chlorochromate (PCC) yielded a product (2 mg) identical with **1** (TLC, $[\alpha]_D$, ^1H NMR, EIMS).

3α-Hydroxy-5α-cycloart-24-en-23-one (**3**). Crystals (16 mg). Mp 111–113° (from Me_2CO). TLC: R_f 0.21 (S-1), 0.41 (S-2); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +15° (*c* 0.4). UV λ_{max} nm (log ε): 232 (3.97). IR ν_{max} cm^{-1}: 3623, 1681, 1616. ^1H NMR: δ 0.35 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.52 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.78 (1H, *dddd*, $J_1 = J_2 = J_3$ = 12.5, J_4 = 2.5 Hz, H-6β), 0.88 (3H, *d*, *J* = 6.5 Hz, Me-21), 0.88 (3H, *s*, Me-31), 0.91 (3H, *s*, Me-32), 0.95 (3H, *s*, Me-30), 1.02 (3H, *s*, Me-18), 1.88 (3H, *d*, *J* = 1.2 Hz, Me-27), 2.10 (1H, *dd*, J_1 = 15, J_2 = 10 Hz, H-22$_B$), 2.15 (3H, *d*, *J* = 1.2 Hz, Me-26), 2.51 (1H, *dd*, J_1 = 15, J_2 = 2.5 Hz, H-22$_A$), 3.46 (1H, *br s*, H-3β), 6.06 (1H, *m*, H-24). ^{13}C NMR: Table 3.

EIMS *m/z* (rel. int.): 440.3655 $[M]^+$ (calcd for $C_{30}H_{48}O_2$: 440.3654) (6), 425 (5), 422 (3), 407 (2), 342 (26), 327 (14), 324 (8), 315 (14), 309 (7), 300 (5), 175 (18), 125 (52), 98 (12), 83 (100).

Compound **1** *by oxidation of* **3**. PCC-oxidation of **3** (1.8 mg) yielded a product (1.6 mg) identical with **1** (TLC, $[\alpha]_D$, ^{1}H NMR, EIMS).

3-*Oxo*-5α-*cycloart*-24-*en*-21-*al* (**4**). Crystals (9 mg). Mp 80–82° (from Me_2CO). TLC: R_f 0.32 (S-1), 0.53 (S-2); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +20° (*c* 0.72). CD (EtOH) nm (Δε): 290 (−0.4), 316 (+0.1). IR ν_{max} cm^{-1}: 1717, 1702. ^{1}H NMR: δ 0.55 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.79 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.92 (3H, *s*, Me-32), 0.95 (1H, *dddd*, $J_1 = J_2 = J_3 = 12.5$, $J_4 = 2.5$ Hz, H-6β), 1.02 (3H, *s*, Me-18), 1.04 (3H, *s*, Me-30), 1.09 (3H, *s*, Me-31), 1.57 (3H, *br s*, Me-26), 1.68 (3H, *br s*, Me-27), 2.30 (1H, *ddd*, $J_1 = 14$, $J_2 = 4.5$, $J_3 = 2.5$ Hz, H-2α), 2.71 (1H, *ddd*, $J_1 = J_2 = 14$, $J_3 = 6.5$ Hz, H-2β), 5.05 (1H, *tqq*, $J_1 = 7$, $J_2 = J_3 = 1.2$ Hz, H-24), 9.46 (1H, *d*, *J* = 5.5 Hz, H-21). ^{13}C NMR: Table 3. EIMS *m/z* (rel. int.): 438.3498 $[M]^+$ (calcd for $C_{30}H_{46}O_2$: 438.3498) (24), 423 (3), 356 (16), 313 (7), 312 (16), 300 (6), 297 (8), 287 (29), 219 (24), 218 (16), 175 (36), 107 (78), 95 (92), 81 (66), 69 (100).

3β-*Hydroxy*-5α-*cycloart*-24-*en*-21-*al* (**5**). Crystals (17 mg). Mp 79–81° (from Me_2CO). TLC: R_f 0.36 (S-2), 0.49 (S-3), 0.62 (S-4); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +47° (*c* 0.28). IR ν_{max} cm^{-1}: 3613, 1718. ^{1}H NMR: δ 0.30 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.56 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.80 (1H, *dddd*, $J_1 = J_2 = J_3 = 12.5$, $J_4 = 2.5$ Hz, H-6β), 0.80 (3H, *s*, Me-31), 0.90 (3H, *s*, Me-32), 0.96 (3H, *s*, Me-30), 0.99 (3H, *s*, Me-18), 1.57 (3H, *br s*, Me-26), 1.67 (3H, *br s*, Me-27), 3.28 (1H, *m*, H-3α), 5.05 (1H, *tqq*, $J_1 = 7$, $J_2 = J_3 = 1.2$ Hz, H-24), 9.46 (1H, *d*, *J* = 5.5 Hz, H-21). ^{13}C NMR: Table 3. EIMS *m/z* (rel. int.): 440.3651 $[M]^+$ (calcd for $C_{30}H_{48}O_2$: 440.3654) (6), 422 (19), 407 (22), 379 (14), 358 (20), 340 (16), 300 (9), 288 (12), 218 (45), 175 (59), 107 (91), 95 (88), 81 (100), 69 (87).

Compound **4** *by oxidation of* **5**. PCC-oxidation of **5** (2 mg) gave a product (0.9 mg) identical with **4** (TLC, $[\alpha]_D$, ^{1}H NMR, EIMS).

5α-*Cycloart*-24-*en*-3β,21-*diol* (**6**). Crystals (121 mg). Mp 130° (from $CHCl_3$). TLC: R_f 0.16 (S-2), 0.44 (S-4); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +41° (*c* 0.96). IR ν_{max} cm^{-1}: 3628. ^{1}H NMR: δ 0.34 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.56 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.80 (1H, *dddd*, $J_1 = J_2 = J_3 = 12.5$, $J_4 = 2.5$ Hz, H-6β), 0.81 (3H, *s*, Me-31), 0.91 (3H, *s*, Me-32), 0.97 (3H, *s*, Me-30), 0.99 (3H, *s*, Me-18), 1.61 (3H, *br s*, Me-26), 1.69 (3H, *br s*, Me-27), 3.29 (1H, *m*, H-3α), 3.62 (1H, *dd*, $J_1 = 11$, $J_2 = 5$ Hz, H-21$_B$), 3.73 (1H, *dd*, $J_1 = 11$, $J_2 = 3$ Hz, H-21$_A$), 5.12 (1H, *tqq*, $J_1 = 7$, $J_2 = J_3 = 1.2$ Hz, H-24). ^{13}C NMR: Table 3. EIMS *m/z* (rel. int.): 442.3812 $[M]^+$ (calcd for $C_{30}H_{50}O_2$: 442.3810) (7), 424 (17), 409 (14), 381 (5), 302 (23), 175 (26), 109 (100), 95 (80), 69 (97).

5α-*Cycloart*-24-*ene*-3β,21-*diyl diacetate*. Acetylation of **6** (10 mg) gave its diacetyl ester. Amorphous (8 mg). TLC: R_f 0.53 (S-2); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +41° (*c* 0.88). IR ν_{max} cm^{-1}: 1724. ^{1}H NMR: δ 0.34 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.58 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.85 (3H, *s*, Me-31), 0.89 (3H, *s*, Me-30), 0.91 (3H, *s*, Me-32), 0.99 (3H, *s*, Me-18), 1.60 (1H, *br s*, Me-26), 1.69 (3H, *br s*, Me-27), 2.05 (6H, *s*, 2 × OCOMe), 3.93 (1H, *dd*, $J_1 = 11$, $J_2 = 5.5$ Hz, H-21$_B$), 4.22 (1H, *dd*, $J_1 = 11$, $J_2 = 3.5$ Hz, H-21$_A$), 4.56 (1H, *dd*, $J_1 = 11$, $J_2 = 5$ Hz, H-3α), 5.09 (1H, *tqq*, $J_1 = 7$, $J_2 = J_3 = 1.2$ Hz, H-24). ^{13}C NMR: δ 15.1 (C-31), 17.6 (C-26), 18.1 (C-18), 19.3 (C-32), 20.0 (C-9), 20.9, 21.0, 21.3 (C-6, 2 × OCO<u>Me</u>), 24.7, 25.4, 25.7, 25.8, 26.0, 26.4 (C-7, C-10, C-11, C-23, C-27, C-30), 26.8 (C-2), 27.6 (C-16), 29.7 (C-19), 30.2 (C-22), 31.6, 31.7 (C-1, C-12), 35.4 (C-15), 39.4 (C-4, C-20), 45.1 (C-13), 46.6 (C-17), 47.1 (C-5), 47.7 (C-8), 48.9 (C-14), 64.9 (C-21), 80.6 (C-3), 124.6 (C-24), 131.4 (C-25), 171.0, 171.4 (2 × O<u>C</u>OMe). EIMS *m/z* (rel. int.): 526 $[M]^+$ (15), 466 (85), 451 (26), 423 (25), 344 (21), 202 (20), 203 (24), 147 (26), 133 (27), 121 (36), 119 (24), 109 (43), 107 (33), 82 (100), 69 (56).

Compound **4** *by oxidation of* **6**. PCC-oxidation of **6** (2 mg) followed by CC (silica gel, petrol–Me_2CO, 49:1) yielded a product (0.9 mg) identical with **4** (TLC, $[\alpha]_D$, ^{1}H NMR, EIMS).

3β-*Hydroxy*-5α-*cycloart*-24-*en*-21-*oic acid* (**7**). Crystals (6 mg). Mp 181° (from $CHCl_3$). TLC: R_f 0.36 (S-3), 0.48 (S-4); anisaldehyde reagent: violet. $[\alpha]_D^{21}$ +23° (*c* 0.48). IR ν_{max} cm^{-1}: 3610, 1702. ^{1}H NMR: δ 0.28 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.56 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.80 (3H, *s*, Me-31), 0.89 (3H, *s*, Me-32), 0.96 (3H, *s*, Me-30), 1.05 (3H, *s*, Me-18), 1.58 (3H, *br s*, Me-26), 1.67 (3H, *br s*, Me-27), 2.16 (1H, *m*), 2.33 (1H, *m*), 3.27 (1H, *m*, H-3α), 5.08 (1H, *tqq*, $J_1 = 7$, $J_2 = J_3 = 1.2$ Hz, H-24). ^{13}C NMR (100 MHz): Table 3. EIMS *m/z* (rel. int.): 456.3605 $[M]^+$ (calcd for $C_{30}H_{48}O_3$: 456.3603) (8), 438 (29), 423 (37), 395 (17), 369 (10), 316 (36), 203 (28), 189 (22), 175 (57), 107 (100), 95 (100), 83 (84), 69 (73).

Reduction of compound **7**. To **7** (2 mg) in MeOH (2 ml) excess CH_2N_2 soln was added. After standing overnight at room temp. the soln was evapd and the residue subjected to $LiAlH_4$-reduction to give a product (1 mg) identical with **6** (TLC, $[\alpha]_D$, ^{1}H NMR, EIMS).

(21RS,23R)-21,23-*Epoxy*-5α-*cycloart*-24-*ene*-3β,21-*diol* (**8**) [*mixture of the* 21-*epimers* **a** and **b** in a 3:2 ratio (in $CDCl_3$–CD_3OD, 1:1)]. Amorphous (31 mg). TLC: R_f 0.20 (S-2), 0.37 (S-3), 0.40 (S-4); anisaldehyde reagent: blue. IR ν_{max} cm^{-1}: 3605, 1602. ^{1}H NMR (in $CDCl_3$–CD_3OD, 1:1): δ 0.32, 0.34 (each 1H, *d*, *J* = 4.2 Hz, H-19$_B$a, H-19$_B$b), 0.58 (2H, *d*, *J* = 4.2 Hz, H-19$_A$a and H-19$_A$b), 0.80 (6H, *s*, Me-31a and Me-31b), 0.92 (6H, *s*, Me-32a and Me-32b), 0.95 (6H, *s*, Me-30a and Me-30b), 1.03, 1.07 (each 3H, *s*, Me-18a, Me-18b), 1.69, 1.72 (each 6H, *br s*, Me-26a and Me-26b, Me-27a and Me-27b), 2.25 (1H, *m*, H-20b), 3.26 (2H, *m*, H-3αa and H-3αb), 4.79 (1H, *ddd*, $J_1 = 9$, $J_2 = J_3 = 7.5$ Hz, H-23b), 4.92 (1H, *ddd*, $J_1 = J_2 = 9$, $J_3 = 2.5$ Hz, H-23a), 5.22 (1H, *dqq*, $J_1 = 9$, $J_2 = J_3 = 1.2$ Hz, H-24a), 5.25 (1H, *d*, *J* = 2 Hz, H-21b), 5.29–5.33 (2H, *m*, H-24b, H-21a). ^{13}C NMR: Table 3. EIMS *m/z* (rel. int.): 456.3605 $[M]^+$ (calcd for $C_{30}H_{48}O_3$: 456.3603) (9), 438 (56), 423 (34), 405 (10), 395 (29), 323 (20), 316 (56), 301 (18), 298 (17), 227 (27), 201 (23), 187 (33), 175 (45), 161 (38), 159 (38), 149 (34), 147 (43), 145 (36), 135 (43), 133 (57), 131 (33), 123 (37), 121 (52), 119 (58), 109 (44), 107 (69), 105 (58), 95 (100), 85 (75), 69 (81).

Compound **9** *by reduction of* **8**. Reduction of **8** with $LiAlH_4$ and purification of the product by CC (silica gel, petrol–Me_2CO, 4:1) yielded a substance (1.3 mg) identical with **9** (mp, TLC, $[\alpha]_D$, ^{1}H NMR, EIMS).

Acetylation of **8**. Compound **8** (20 mg) was acetylated and the product separated by HPLC (silica gel, petrol–EtOH, 99:1) to yield the acetylated 21-epimers **33** and **34**.

(21S,23R)-21,23-*Epoxy*-5α-*cycloart*-24-*ene*-3β,21α-*diyl diacetate* (**33**). Crystals (9 mg). Mp 159–161° (from petrol). TLC: R_f 0.44 (S-2), 0.68 (S-4); anisaldehyde reagent: blue. $[\alpha]_D^{21}$ −9° (*c* 0.24). IR ν_{max} cm^{-1}: 1727. ^{1}H NMR: δ 0.31 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.60 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.84 (3H, *s*, Me-31), 0.88 (3H, *s*, Me-30), 0.91 (3H, *s*, Me-32), 1.02 (3H, *s*, Me-18), 1.67, 1.70 (each 3H, *d*, *J* = 1.2 Hz, Me-26, Me-27), 2.04, 2.06 (each 3H, *s*, 2 × OCOMe), 2.23 (1H, *m*, H-20), 4.56 (1H, *dd*, $J_1 = 11$, $J_2 = 4.5$ Hz, H-3α), 4.90 (1H, *ddd*, $J_1 = J_2 = 9$, $J_3 = 2$ Hz, H-23), 5.22 (1H, *dqq*, $J_1 = 9$, $J_2 = J_3 = 1.2$ Hz, H-24), 6.20 (1H, *d*, *J* = 4 Hz, H-21β). ^{13}C NMR (100 MHz): δ 15.1 (C-31), 18.1 (C-26), 19.0 (C-18), 19.2 (C-32), 20.0 (C-9), 20.6 (C-6), 21.4, 21.5 (2 × OCO<u>Me</u>), 25.4 (C-30), 25.7, 25.7, 26.2, 26.4 (C-7, C-10, C-11, C-27), 26.7 (C-2), 27.7 (C-16), 29.7 (C-19), 30.7 (C-12), 31.5 (C-1), 35.5 (enhanced) (C-15, C-22), 39.4 (C-4), 45.2, 45.2 (C-17, C-20), 46.9 (C-5), 47.4 (C-8), 48.5 (C-14), 74.9 (C-23), 80.6 (C-3), 97.0 (C-21), 126.1 (C-24), 135.2 (C-25), 170.5, 171.0 (2 × O<u>C</u>OMe). EIMS *m/z* (rel. int.): 480 $[M-60]^+$ (26), 420 (3), 298 (12), 187 (14), 175 (9), 150 (100), 135 (30), 133 (20), 123 (67), 121 (24), 119 (26), 107 (63), 95 (40), 43 (41). DCIMS (isobutane) *m/z* (rel. int.): 540 $[M]^+$ (2), 481 $[M+1$

$-60]^+$ (100), 421 $[M+1-60-60]^+$ (100).

(21R,23R)-21,23-*Epoxy*-5α-*cycloart*-24-*ene*-3β,21β-*diyl diacetate* (**34**). Crystals (7 mg). Mp 158–159° (from petrol). TLC: R_f 0.46 (S-2), 0.70 (S-4); anisaldehyde reagent: blue. $[\alpha]_D^{21}$ +41° (*c* 0.45). IR ν_{max} cm^{-1}: 1724. ^1H NMR: δ0.36 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.58 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.84 (3H, *s*, Me-31), 0.88 (3H, *s*, Me-30), 0.92 (3H, *s*, Me-32), 1.04 (3H, *s*, Me-18), 1.69, 1.73 (each 3H, *d*, *J* = 1.2 Hz, Me-26, Me-27), 2.04, 2.05 (each 3H, *s*, 2 × OCOMe), 2.37 (1H, *m*, H-20), 4.57 (1H, *dd*, J_1 = 11, J_2 = 4.5 Hz, H-3α), 4.92 (1H, *ddd*, J_1 = 9, $J_2 \sim J_3 \sim$ 7.5 Hz, H-23), 5.21 (1H, *dqq*, J_1 = 9, $J_2 = J_3$ = 1.2 Hz, H-24), 6.20 (1H, *s*, H-21α). ^{13}C NMR (100 MHz): δ15.1 (C-31), 18.1 (C-26), 18.7 (C-18), 19.3 (C-32), 20.0 (C-9), 20.8 (C-6), 21.3, 21.6 (2 × OCOMe), 25.4 (C-30), 25.8, 25.9, 26.0, 26.2 (C-7, C-10, C-11, C-27), 26.8 (C-2), 27.7 (C-16), 29.7 (C-19), 31.5 (C-1), 31.8 (C-12), 35.2, 35.3 (C-15, C-22), 39.4 (C-4), 45.3 (C-13), 46.4 (C-20), 47.1 (C-5), 47.8 (C-8), 48.7 (C-14), 49.1 (C-17), 76.9 (C-23), 80.6 (C-3), 101.0 (C-21), 126.7 (C-24), 136.0 (C-25), 170.5, 171.0 (2 × OCOMe). EIMS *m/z* (rel. int.): 480 $[M-60]^+$ (8), 420 (< 1), 175 (4), 150 (100), 135 (20), 107 (43), 95 (22), 43 (27). DCIMS (isobutane) *m/z* (rel. int.): 497 $[M-43]^+$ (8), 481 $[M+1-60]^+$ (37), 421 $[M+1-60-60]^+$ (100), 393 (22).

(23R)-3-*Oxo*-5α-*cycloart*-24-*en*-21,23-*olide* (**35**). Compound **8** (3 mg) was oxidized by PCC and the product purified by HPLC (silica gel; petrol–EtOH, 99 : 1) to give **35** as crystals (2.5 mg). Mp 180–181° (from Me_2CO). TLC: R_f 0.21 (S-1), 0.42 (S-2), 0.57 (S-4); anisaldehyde reagent: blue. $[\alpha]_D^{21}$ −14° (*c* 0.15). CD nm (Δε): 220 (+0.9), 290 (−0.7). IR ν_{max} cm^{-1}: 1760, 1699. ^1H NMR: δ0.57 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.81 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.95 (3H, *s*, Me-32), 1.05 (3H, *s*, Me-30), 1.10 (3H, *s*, Me-31), 1.14 (3H, *s*, Me-18), 1.75, 1.77 (each 3H, *d*, *J* = 1.2 Hz, Me-26, Me-27), 2.25 (1H, *m*), 2.31 (1H, *ddd*, J_1 = 14, J_2 = 4.5, J_3 = 2.5 Hz, H-2α), 2.36 (1H, *m*), 2.71 (1H, *ddd*, $J_1 = J_2$ = 14, J_3 = 6.5 Hz, H-2β), 2.71 (1H, *ddd*, $J_1 = J_2$ = 8.5, J_3 = 5 Hz, H-20), 5.18 (1H, *ddd*, J_1 = 8.5, $J_2 = J_3$ = 7 Hz, H-23), 5.22 (1H, *dqq*, J_1 = 8.5, $J_2 = J_3$ = 1.2 Hz, H-24). ^1H NMR (C_6D_6): δ0.15 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.45 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.63 (1H, *dddd*, $J_1 = J_2 = J_3$ = 12.5, J_4 = 2.5 Hz, H-6β), 0.82 (3H, *s*, Me-32), 0.93 (3H, *s*, Me-30), 1.16 (3H, *s*, Me-18), 1.19 (3H, *s*, Me-31), 1.44, 1.52 (each 3H, *d*, *J* = 1.2 Hz, Me-26, Me-27), 2.00 (1H, *m*), 2.26 (1H, *ddd*, J_1 = 14, J_2 = 4.5, J_3 = 2.5 Hz, H-2α), 2.32 (1H, *m*, H-17), 2.43 (1H, *ddd*, $J_1 = J_2$ = 14, J_3 = 6.5 Hz, H-2β), 2.51 (1H, *ddd*, $J_1 = J_2$ = 8.5, J_3 = 5 Hz, H-20), 5.01 (1H, *ddd*, J_1 = 8.5, $J_2 = J_3$ = 7 Hz, H-23), 5.11 (1H, *dqq*, J_1 = 8.5, $J_2 = J_3$ = 1.2 Hz, H-24); NOE and COSY measured in C_6D_6. ^{13}C NMR (100 MHz): δ18.4 (C-26), 19.0 (C-18), 19.4 (C-32), 20.8 (C-31), 21.0 (C-9), 21.3 (C-6), 22.2 (C-30), 25.8, 25.9 (C-7, C-10), 26.2, 26.4, 26.5 (C-11, C-16, C-27), 29.7 (C-19), 30.2 (C-12), 33.3 (C-1), 34.6 (C-22), 35.1 (C-15), 37.4 (C-2), 41.3 (C-20), 45.6 (C-13), 47.0 (C-17), 47.8 (C-8), 48.3 (C-5), 48.5 (C-14), 50.2 (C-4), 75.0 (C-23), 123.3 (C-24), 139.4 (C-25), 178.9 (C-21), 216.5 (C-3). EIMS *m/z* (rel. int.): 452 $[M]^+$ (23), 437 (11), 397 (12), 314 (27), 119 (21), 107 (24), 105 (22), 83 (100).

(23R)-5α-*Cycloart*-24-*ene*-3β,21,23-*triol* (**9**). Crystals (17 mg). Mp 204–205° (from MeOH). TLC: R_f 0.12 (S-2), 0.22 (S-4); anisaldehyde reagent: violet. $[\alpha]_D^{21}$ +38° (*c* 0.6). IR ν_{max} cm^{-1}: 3611. ^1H NMR: δ0.35 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.56 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.80 (1H, *dddd*, $J_1 = J_2 = J_3$ = 12.5, J_4 = 2.5 Hz, H-6β), 0.81 (3H, *s*, Me-31), 0.93 (3H, *s*, Me-32), 0.97 (3H, *s*, Me-30), 1.01 (3H, *s*, Me-18), 1.70, 1.72 (each 3H, *d*, *J* = 1.2 Hz, Me-26, Me-27), 3.29 (1H, *m*, H-3α), 3.63 (1H, *dd*, J_1 = 11, J_2 = 5 Hz, H-21$_B$), 3.79 (1H, *dd*, J_1 = 11, J_2 = 3 Hz, H-21$_A$), 4.60 (1H, *ddd*, $J_1 = J_2$ = 9, J_3 = 2.5 Hz, H-23), 5.25 (1H, *dqq*, J_1 = 9, $J_2 = J_3$ = 1.2 Hz, H-24). ^{13}C NMR ($CDCl_3$–CD_3OD, 1 : 1): Table 3. EIMS *m/z* (rel. int.): 458.3762 $[M]^+$ (calcd for $C_{30}H_{50}O_3$: 458.3760) (18), 443 (8), 440 (44), 425 (54), 422 (13), 407 (29), 397 (7), 379 (6), 358 (15), 340 (11), 325 (10), 318 (19), 303 (6), 300 (15), 297 (13), 285 (25), 201 (22), 175 (25), 163 (20), 159 (20), 147 (41), 145 (23), 135 (24), 133 (31), 125 (23), 123 (20), 121 (31), 119 (35), 109 (32), 107 (53), 105 (34), 95 (53), 85 (100), 69 (39).

(23R)- *and* (23S)-21,23-*Epoxy*-5α-*cycloart*-24-*en*-3-*one* [**10a** (*major component*)/**10b**] (*mixture of the* 23-*epimers in a* 9 : 1 *ratio*). Amorphous (60 mg). TLC: R_f 0.31 (S-1), 0.52 (S-2); anisaldehyde reagent: lilac. CD nm (Δε): 293 (−0.64). IR ν_{max} cm^{-1}: 1700. ^1H NMR: δ0.56 (2H, *d*, *J* = 4.2 Hz, H-19$_B$a and H-19$_B$b), 0.80 (2H, *d*, *J* = 4.2 Hz, H-19$_A$a and H-19$_A$b), 0.91 (6H, *s*, Me-32a and Me-32b), 1.01 (6H, *s*, Me-18a and Me-18b), 1.05 (6H, *s*, Me-30a and Me-30b), 1.10 (6H, *s*, Me-31a and Me-31b), 1.69, 1.72 (each 6H, *d*, *J* = 1.2 Hz, Me-26a and Me-26b, Me-27a and Me-27b), 2.30 (2H, *ddd*, J_1 = 14, J_2 = 4.5, J_3 = 2.5 Hz, H-2αa and H-2αb), 2.71 (2H, *ddd*, $J_1 = J_2$ = 14, J_3 = 6.5 Hz, H-2βa and H-2βb), 3.21, 3.39 (each 1H, *dd*, J_1 = 9.5, J_2 = 8.5 Hz, H-21$_B$a, H-21$_B$b), 3.95, 4.03 (each 1H, *dd*, J_1 = 8.5, J_2 = 7 Hz, H-21$_A$a, H-21$_A$b), 4.54 (1H, *ddd*, J_1 = 10, J_2 = 8.5, J_3 = 5 Hz, H-23a), 4.60 (1H, *ddd*, J_1 = 8.5, $J_2 = J_3$ = 6.5 Hz, H-23b), 5.19, 5.22 (each 1H, *dqq*, J_1 = 8.5, $J_2 = J_3$ = 1.2 Hz, H-24a, H-24b). ^{13}C NMR (for **10a** only): Table 3. EIMS *m/z* (rel. int.): 438.3498 $[M]^+$ (calcd for $C_{30}H_{46}O_2$: 438.3498) (22), 423 (55), 313 (2), 300 (8), 285 (17), 125 (100), 123 (25), 109 (27), 107 (26), 105 (24), 69 (75).

(23R)-*and* (23S)-21,23-*Epoxy*-5α-*cycloart*-24-*en*-3β-*ol* [**11a** (*major component*)/**11b**] (*mixture of the* 23-*epimers in a* 4 : 1 *ratio*). Amorphous (36 mg). TLC: R_f 0.16 (S-1), 0.40 (S-2), 0.58 (S-4); anisaldehyde reagent: lilac. IR ν_{max} cm^{-1}: 3612. ^1H NMR: δ0.31 (2H, *d*, *J* = 4.2 Hz, H-19$_B$a and H-19$_B$b), 0.57 (2H, *d*, *J* = 4.2 Hz, H-19$_A$a and H-19$_A$b), 0.80 (6H, *s*, Me-31a and Me-31b), 0.89 (6H, *s*, Me-32a and Me-32b), 0.96 (6H, *s*, Me-30a and Me-30b), 0.97 (3H, *s*, Me-18a), 0.99 (3H, *s*, Me-18b), 1.69, 1.72 (each 6H, *d*, *J* = 1.2 Hz, Me-26a and Me-26b, Me-27a and Me-27b), 3.28 (2H, *m*, H-3αa and H-3αb), 3.20, 3.39 (each 1H, *dd*, J_1 = 9.5, J_2 = 8.5 Hz, H-21$_B$a, H-21$_B$b), 3.94, 4.03 (each 1H, *dd*, J_1 = 8.5, J_2 = 7 Hz, H-21$_A$a, H-21$_A$b), 4.53 (1H, *ddd*, J_1 = 10, J_2 = 8.5, J_3 = 5 Hz, H-23a), 4.59 (1H, *ddd*, J_1 = 8.5, $J_2 = J_3$ = 6.5 Hz, H-23b), 5.18, 5.21 (each 1H, *dqq*, J_1 = 8.5, $J_2 = J_3$ = 1.2 Hz, H-24a, H-24b). ^{13}C NMR: Table 3. EIMS *m/z* (rel. int.): 440.3655 $[M]^+$ (calcd for $C_{30}H_{48}O_2$: 440.3654) (35), 425 (68), 422 (17), 407 (26), 379 (20), 353 (7), 300 (36), 285 (92), 182 (20), 175 (14), 161 (22), 147 (23), 135 (21), 133 (20), 125 (100), 123 (31), 121 (23), 119 (24), 109 (35), 107 (43), 105 (29), 69 (70).

Compound **10** *by oxidation of* **11**. PCC-oxidation of **11** (2 mg) gave a product (1.5 mg) identical with **10** (TLC, CD, ^1H NMR, EIMS).

(23S)-21,23-*Epoxy*-5α-*cycloart*-24-*en*-3α-*ol* (**12**). Crystals (10 mg). Mp 166–168° (from MeOH). TLC: R_f 0.42 (S-2), 0.56 (S-3), 0.60 (S-4); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +5° (*c* 0.80). IR ν_{max} cm^{-1}: 3629. ^1H NMR: δ0.27 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.48 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.73 (1H, *dddd*, $J_1 = J_2 = J_3$ = 12.5 Hz, J_4 = 2.5 Hz, H-6β), 0.82 (3H, *s*, Me-31), 0.84 (3H, *s*, Me-32), 0.90 (3H, *s*, Me-30), 0.92 (3H, *s*, Me-18), 1.63, 1.67 (each 3H, *d*, *J* = 1.2 Hz, Me-26, Me-27), 3.33 (1H, *dd*, J_1 = 9.5, J_2 = 8 Hz, H-21$_B$), 3.42 (1H, *m*, H-3α), 3.89 (1H, *dd*, J_1 = 8, J_2 = 7.5 Hz, H-21$_A$), 4.48 (1H, *ddd*, J_1 = 10, J_2 = 8.5, J_3 = 5 Hz, H-23), 5.13 (1H, *dqq*, J_1 = 8.5, $J_2 = J_3$ = 1.2 Hz, H-24). ^{13}C NMR (100 MHz): Table 3. EIMS *m/z* (rel. int.): 440.3659 $[M]^+$ (calcd for $C_{30}H_{48}O_2$: 440.3654) (100), 425 (94), 422 (13), 407 (13), 300 (14), 285 (34), 175 (16), 125 (98).

Compound **10** *by oxidation of* **12**. PCC-oxidation of **12** (2 mg) gave a product (1.3 mg) identical with **10** (TLC, CD, ^1H NMR, EIMS).

(21R,24R)-21,24-*Cyclo*-5α-*cycloartane*-3β,21,25-*triol* (**13**). Crystals (8 mg). Mp 177–178° (from MeOH). TLC: R_f 0.14 (S-2), 0.33 (S-3), 0.28 (S-4); anisaldehyde reagent: blue. $[\alpha]_D^{21}$ +30° (*c* 0.15). IR ν_{max} cm^{-1}: 3613, 3460 br. ^1H NMR: δ0.31 (1H, *d*, *J* = 4.2 Hz, H-19$_B$), 0.57 (1H, *d*, *J* = 4.2 Hz, H-19$_A$), 0.80 (3H, *s*,

Me-31), 0.81 (1H, *dddd*, $J_1=J_2=J_3=12.5$, $J_4=2.5$ Hz, H-6β), 0.92 (3H, *s*, Me-32), 0.97 (3H, *s*, Me-30), 1.03 (3H, *s*, Me-18), 1.20, 1.23 (each 3H, *s*, Me-26, Me-27), 2.7 (1H, *br s*, OH), 3.28 (1H, *m*, H-3α), 3.72 (1H, *dd*, $J_1=8.5$, $J_2=7$ Hz, H-21). ^{13}C NMR: Table 3. EIMS *m/z* (rel. int.): 458.3761 $[M]^+$ (calcd for $C_{30}H_{50}O_3$: 458.3760) (2), 443 (3), 440 (9), 425 (10), 422 (6), 407 (8), 318 (21), 300 (10), 281 (11), 227 (22), 203 (24), 187 (24), 175 (40), 174 (37), 173 (31), 161 (33), 159 (41), 149 (28), 148 (22), 147 (52), 145 (42), 135 (37), 133 (50), 132 (22), 131 (30), 123 (21), 121 (55), 120 (27), 119 (63), 117 (21), 109 (60), 108 (23), 107 (85), 106 (21), 105 (67), 95 (90), 81 (65), 69 (72), 59 (100), 55 (68), 43 (82).

(21R,24R)-21,25-*Dihydroxy*-21,24-*cyclo*-5α-*cycloartan*-3-*one* (**14**). Crystals (6 mg). Mp 203–204° (from MeOH). TLC: R_f 0.39 (S-2), 0.49 (S-3), 0.38 (S-4); anisaldehyde reagent: violet. $[\alpha]_D^{21}$ +18° (*c* 0.48). CD nm ($\Delta\varepsilon$): 293 (−0.53). IR ν_{max} cm^{-1}: 3611, 3511 br, 1699. ^{1}H NMR: δ 0.56 (1H, *d*, $J=4.2$ Hz, H-19$_B$), 0.81 (1H, *d*, $J=4.2$ Hz, H-19$_A$), 0.93 (3H, *s*, Me-32), 1.05 (3H, *s*, Me-30), 1.07 (3H, *s*, Me-18), 1.10 (3H, *s*, Me-31), 1.21, 1.24 (each 3H, *s*, Me-26, Me-27), 2.05 (1H, *m*), 2.30 (1H, *ddd*, $J_1=14$, $J_2=4.5$, $J_3=2.5$ Hz, H-2α), 2.71 (1H, *ddd*, $J_1=J_2=14$, $J_3=6.5$ Hz, H-2β), 3.73 (1H, *dd*, $J_1=8.5$, $J_2=7$ Hz, H-21). ^{13}C NMR: Table 3. EIMS *m/z* (rel. int.): 456.3601 $[M]^+$ (calcd for $C_{30}H_{48}O_3$: 456.3603) (3), 438 (47), 423 (16), 420 (29), 405 (9), 380 (9), 341 (15), 318 (11), 313 (27), 312 (28), 300 (12), 297 (18), 219 (29), 201 (23), 175 (25), 174 (20), 173 (21), 161 (21), 159 (28), 147 (38), 145 (31), 135 (26), 133 (39), 131 (23), 121 (41), 120 (21), 119 (45), 109 (47), 108 (27), 107 (62), 105 (45), 43 (100).

Compound **13** *by reduction of* **14**. Compound **14** (2 mg) on reduction with $LiAlH_4$ and purification by CC (silica gel, petrol–Me_2CO, 8:2) gave a product (1.3 mg) identical with **13** (TLC, $[\alpha]_D$, ^{1}H NMR, EIMS).

(20R)-3β-*Hydroxy*-24,25,26,27-*tetranor*-5α-*cycloartan*-23,21-*olide* (**15**). Crystals (9 mg). Mp 219–220° (from Me_2O). TLC: R_f 0.19 (S-2), 0.37 (S-3), 0.47 (S-4); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +48° (*c* 0.7). CD nm ($\Delta\varepsilon$): 217 (+0.76). IR ν_{max} cm^{-1}: 3614, 1774. ^{1}H NMR (360 MHz): δ 0.34 (1H, *d*, $J=4.2$ Hz, H-19$_B$), 0.59 (1H, *d*, $J=4.2$ Hz, H-19$_A$), 0.81 (1H, *dddd*, $J_1=J_2=J_3=12.5$, $J_4=2.5$ Hz, H-6β), 0.81 (3H, *s*, Me-31), 0.91 (3H, *s*, Me-32), 0.97 (3H, *s*, Me-30), 1.01 (3H, *s*, Me-18), 2.19 (1H, *m*, H-22$_B$), 2.49–2.63 (2H, *m*, H-20, H-22$_A$), 3.28 (1H, *m*, H-3α), 3.89 (1H, *dd*, $J_1=J_2=9$ Hz, H-21$_B$), 4.42 (1H, *dd*, $J_1=9$, $J_2=8$ Hz, H-21$_A$). ^{13}C NMR (90 MHz): Table 3. EIMS *m/z* (rel. int.): 400.2979 $[M]^+$ (calcd for $C_{26}H_{40}O_3$: 400.2977) (6), 385 (20), 382 (46), 368 (20), 367 (71), 339 (100), 313 (35), 297 (11), 175 (16), 135 (22), 133 (26), 121 (21), 119 (38), 107 (34), 105 (25).

(20R)-3-*Oxo*-24,25,26,27-*tetranor*-5α-*cycloartan*-23,21-*olide by oxidation of* **15**. PCC-oxidation of **15** (3 mg) and subsequent purification of the product by CC on silica gel (petrol–Me_2CO, 9:1) gave the title compound (2.5 mg). Mp 200–203° (from Me_2CO). TLC: R_f 0.47 (S-3); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ +21° (*c* 0.2). CD nm ($\Delta\varepsilon$): 217 (+0.86), 294 (−0.70). IR ν_{max} cm^{-1}: 1775, 1700. ^{1}H NMR: δ 0.58 (1H, *d*, $J=4.2$ Hz, H-19$_B$), 0.82 (1H, *d*, $J=4.2$ Hz, H-19$_A$), 0.93 (3H, *s*, Me-32), 1.04 (3H, *s*, Me-18), 1.05 (3H, *s*, Me-30), 1.10 (3H, *s*, Me-31), 2.21 (1H, *m*, H-22$_B$), 2.31 (1H, *ddd*, $J_1=14$, $J_2=4.5$, $J_3=2.5$ Hz, H-2α), 2.51–2.65 (2H, *m*, H-20, H-22$_A$), 2.71 (1H, *ddd*, $J_1=J_2=14$, $J_3=6.5$ Hz, H-2β), 3.89 (1H, *dd*, $J_1=J_2=9$ Hz, H-21$_B$), 4.43 (1H, *dd*, $J_1=9$, $J_2=8$ Hz, H-21$_A$). EIMS *m/z* (rel. int.) : 398 $[M]^+$ (100), 384 (20), 383 (77), 365 (11), 355 (6), 313 (4), 312 (4), 260 (17), 119 (23), 107 (34), 105 (36).

Eupha-8,24-*dien*-3β-*ol* (**16**). Crystals (2 mg). Mp 114–116° (from Me_2CO) (ref. [5] mp 116–117°). $[\alpha]_D^{21}$ +27° (*c* 0.6) (ref. [5] $[\alpha]_D$ +31° (*c* 1.2)). ^{1}H NMR, ^{13}C NMR, EIMS in agreement with published data [5, 6].

Mixture of 7-*oxostigmast*-5-*en*-3β-*yl oleate and palmitate* (**17a** and **17b**). Amorphous (11 mg). TLC R_f 0.56 (S-1); anisaldehyde reagent: blue. UV λ_{max} nm (log ε): 227 (3.90). IR ν_{max} cm^{-1}: 1727, 1669. ^{1}H NMR: δ 0.68 (3H, *s*, Me-18), 0.81, 0.83 (each 3H, *d*, $J=6.5$ Hz, Me-26, Me-27), 0.84 (3H, *t*, $J=7$ Hz, Me-29), 0.88 (3H, *t*, $J=7$ Hz, Me-ω), 0.93 (3H, *d*, $J=6.5$ Hz, Me-21), 1.21 (3H, *s*, Me-19), 4.72 (1H, *m*, H-3), 5.35 (2H, *m*, CH_2-HC=CH-CH_2), 5.70 (1H, *d*, $J=1.5$ Hz, H-6). ^{13}C NMR from sterol moiety: δ 12.1 (C-18 and C-29), 17.4 (C-19), 19.1, 19.2 (C-21, C-26), 19.8 (C-27), 21.4 (C-11), 23.4 (C-28), 26.4 (C-25), 26.7 (C-15), 27.6 (C-2), 28.5 (C-16), 29.3 (C-23), 34.3 (C-22), 36.2, 36.3 (C-1, C-20), 38.0 (C-4), 38.5 (C-10), 39.0 (C-12), 43.4 (C-13), 45.7 (C-8), 46.3 (C-24), 50.2, 50.3 (C-9, C-14), 55.2 (C-17), 72.1 (C-3), 126.8 (C-6), 163.6 (C-5), 201.3 (C-7); fatty acid moieties: δ 13.9 (Me), 22.7, 25.1, 27.2, 27.3, 29.2, 29.5, 29.7, 29.8, 32.0 [–$(CH_2)_n$–], 34.6 (C-2'), 129.8, 130.1 (CH_2–HC=CH–CH_2), 172.8 (C-1'). EIMS *m/z* (rel. int.): 412 (36), 411 (100), 410 (19), 174 (35). DCIMS (isobutane) *m/z* (rel. int.): 693 $[M^a+1]^+$ (1), 667 $[M^b+1]^+$ (0.5), 412 (32), 411 (100), 283 (43), 257 (39).

Methanolysis of **17a** *and* **17b**. The mixture of **17a** and **17b** (4 mg) was stirred in 10% NaOMe–MeOH (1 ml) for 2 hr. H_2O was added and the product extracted with CH_2Cl_2. Removal of the solvent and subsequent CC on silica gel (petrol–Me_2CO, 9:1) yielded: (a) 3β-hydroxystigmast-5-en-7-one (amorphous, 1.5 mg) and (b) a mixture of the methyl esters of oleic acid (75%) and palmitic acid (25%). The 3β-hydroxystigmast-5-en-7-one was identified by TLC: R_f 0.19 (S-2); anisaldehyde reagent: lilac. $[\alpha]_D^{21}$ −57° (*c* 0.26) (lit. [36] $[\alpha]_D^{26}$ −65° (*c* 0.85)). UV, IR, ^{1}H NMR, EIMS in agreement with published data [36, 37]. Identification of the methyl esters was achieved by GC comparison (capillary column, SE 54, 25 m; 120→280°) of the mixture of esters with authentic compounds and by GC-MS.

Sitosterol (**18**). Crystals (11 mg). Mp 137–138° (from Me_2CO). $[\alpha]_D^{21}$ −38° (*c* 1.0). IR, ^{1}H, ^{13}C NMR, EIMS identical with an authentic sample.

Stigmasterol (**19**). Crystals (7 mg). Mp 164–166° (from Me_2CO). $[\alpha]_D^{21}$ −47° (*c* 0.6). IR, ^{1}H, ^{13}C NMR, EIMS identical with an authentic sample.

T-Cadinol (**20**). Oil (9 mg). $[\alpha]_D^{21}$ +4° (*c* 0.7) (ref. [12] $[\alpha]_D^{21}$ +3.4° (*c* 1.2)). ^{1}H NMR, EIMS in agreement with published data [11, 12].

The corresponding CC fraction containing a mixture of mainly **21** and **23** was subjected to prep. GC using a Perkin-Elmer F21 on Volaspher® A 2 (80–100 mesh) coated with 4% SE 30 (1.8 m × 8 mm). Temp. program: 130° isotherm; flow: *ca* 500 ml N_2 min^{-1}. Compounds **21** and **23** eluted after 10.5 and 15.0 min, respectively.

β-Caryophyllene (**21**). Oil (13 mg). $[\alpha]_D^{21}$ −12° (*c* 0.3). IR, ^{1}H NMR, ^{13}C NMR, EIMS identical with an authentic sample.

α-Copaene (**23**). Oil (3 mg). $[\alpha]_D^{21}$ −6° (*c* 0.4) (ref. [14] $[\alpha]_D^{30}$ −6.5° (*c* 2.3)). ^{1}H NMR, EIMS in agreement with published data [14, 42].

Caryophyllene oxide (**22**). Oil (95 mg). $[\alpha]_D^{21}$ −48° (*c* 1.1). IR, ^{1}H NMR, ^{13}C NMR, EIMS identical with an authentic sample.

α-Cyperone (**24**). Oil (3 mg). $[\alpha]_D^{21}$ +102° (*c* 0.1) (ref. [15] $[\alpha]_D$ +103.5° (*c* 1.5)). ^{1}H, ^{13}C NMR, EIMS in agreement with published data [15, 43, 44].

Elemol (**25**). Oil (5 mg). $[\alpha]_D^{21}$ −4° (*c* 0.4) (ref. [16] $[\alpha]_D$ −4.6° (*c* 0.5)). ^{1}H, ^{13}C NMR, EIMS in agreement with published data [16, 17].

α-Eudesmol (**26**). Crystals (2 mg). Mp 74–75° (from petrol) (ref. [18] mp 74–75°). $[\alpha]_D^{21}$ +25° (*c* 0.2) (ref. [18] $[\alpha]_D^{25}$ +28.5° (*c* 1.2)). ^{1}H NMR, EIMS in agreement with published data [18, 45].

β-Eudesmol (**27**). Crystals (107 mg). Mp 79–80° (from petrol) (ref. [18] mp 79–80°). $[\alpha]_D^{21}$ +58° (*c* 0.2). (ref. [18] $[\alpha]_D^{25}$ +56.6° (*c* 2.0)). ^{1}H NMR, EIMS in agreement with published data [18, 45].

Geranic acid (**28**). Oil (1.6 g). Identification via its methyl ester

(by treatment with CH_2N_2). ^1H, ^{13}C NMR in agreement with published data [19, 20].

Elemicin (**29**). Oil (13 mg). ^{13}C NMR: δ 40.5 (C-1'), 56.4 (MeO-1, MeO-3), 60.7 (MeO-2), 106.6 (C-4, C-6), 115.8 (C-3'), 135.7 (C-5), 137.3 (C-2, C-2'), 153.5 (C-1, C-3). ^1H NMR, EIMS in agreement with published data [21].

(E)-*Isoelemicin* (**30**). Oil (16 mg). ^{13}C NMR: δ 18.1 (C-3'), 56.4 (MeO-1, MeO-3), 60.8 (MeO-2), 104.1 (C-4, C-6), 125.0 (C-2'), 131.2 (C-1'), 133.9 (C-5), 138.3 (C-2), 153.6 (C-1, C-3). ^1H NMR, EIMS in agreement with published data [22].

Acknowledgements—Thanks are due to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

REFERENCES

1. Achenbach, H., Waibel, R., Zwanzger, M., Dominguez, X. A., Espinoza B., G., Verde S., J. and Sánchez V., H. (1992) *J. Nat. Prod.* **55**, 918.
2. Fries, R. (1959) in *Die natürlichen Pflanzenfamilien* (Engler, A., Harms, H., Mattfeld, J. and Werdermann, G., eds), Vol. 17a II, p. 164. Dunker & Humblot, Berlin.
3. Achenbach, H., Frey, D. and Waibel, R. (1991) *J. Nat. Prod.* **54**, 1331.
4. Achenbach, H. and Frey, D. (1989) *Arch. Pharm. (Weinheim)* **322**, 743.
5. Rishi, A. K., George, V. and Kapoor, R. (1979) *Planta Med.* **35**, 193.
6. Kaiser, W. (1987) *An. Acad. Bras. Ci.* **59**, 173.
7. Nishioka, I., Ikekawa, N., Yagi, A., Kawasaki, T. and Tsukamoto, T. (1965) *Chem. Pharm. Bull.* **13**, 379.
8. Chaurasia, N. and Wichtl, M. (1987) *J. Nat. Prod.* **50**, 881.
9. Yanagawa, H., Kato, T., Kitahara, Y. and Kato, Y. (1972) *Phytochemistry* **11**, 1893.
10. Wright, J. L. C., McInnes, A. G., Shimizu, S., Smith, D. G., Walter, J. A., Idler, D. and Khalil, W. (1978) *Can. J. Chem.* **56**, 1898.
11. Cheng, Y. S., Kuo, Y. H. and Lin, Y. T. (1967) *J. Chem. Soc., Chem. Commun.* 565.
12. Borg-Karlson, A.-K., Norin, T. and Talvitie, A. (1981) *Tetrahedron* **37**, 425.
13. De Pascual Teresa, J., Urones, J. G. and Fernandez, A. (1983) *Phytochemistry* **22**, 2753.
14. Kapadia, V. H., Nagasampagi, B. A., Naik, V. G. and Dev, S. (1965) *Tetrahedron* **21**, 607.
15. Roberts, D. L. (1972) *Phytochemistry* **11**, 2077.
16. Kutney, J. P. and Singh, A. K. (1983) *Can. J. Chem.* **61**, 1111.
17. Schmaus, G., Schultze, W. and Kubeczka, K.-H. (1989) *Planta Med.* **55**, 482.
18. Humber, D. C., Pinder, A. R. and Williams, R. A. (1967) *J. Org. Chem.* **32**, 2335.
19. Campbell, R. V. M., Crombie, L., Findley, D. A. R., King, R. W., Pattenden, G. and Whiting, D. A. (1975) *J. Chem. Soc., Perkin Trans. I* 897.
20. Crombie, L., King, R. W. and Whiting, D. A. (1975) *J. Chem. Soc., Perkin Trans. I* 913.
21. Giesbrecht, A. M., Franca, N. C., Gottlieb, O. R. and Da Rocha, A. I. (1974) *Phytochemistry* **13**, 2285.
22. Enqiquez, R. G., Chávez, M. A. and Jáuregui, F. (1980) *Phytochemistry* **19**, 2024.
23. Khuong-Huu, F., Sangare, M., Chari, V. M., Bekaert, A., Devys, M., Barbier, M. and Lukacs, G. (1975) *Tetrahedron Letters* 1787.
24. Kamisako, W., Honda, C., Suwa, K. and Isoi, K. (1987) *Magn. Reson. Chem.* **25**, 683.
25. Bentley, H. R., Henry, J. A., Irvine, D. S. and Spring, F. S. (1953) *J. Chem. Soc.* 3673.
26. Takahashi, K. and Takani, M. (1975) *Chem. Pharm. Bull.* **23**, 538.
27. Anjaneyulu, V., Ravi, K., Harischandra Prasad, K. and Connolly, J. D. (1989) *Phytochemistry* **28**, 1471.
28. Kahlos, K., Hiltunen, R. and von Schantz, M. (1984) *Planta Med.* **50**, 197.
29. Herz, W., Watanabe, K., Kulanthaivel, P. and Blount, J. F. (1985) *Phytochemistry* **24**, 2645.
30. Eliel, E. L., Rao, V. S. and Pietrusiewicz, K. M. (1979) *Org. Magn. Reson.* **12**, 461.
31. Nishida, Y., Ohrui, H., Meguro, H. and Mori, K. (1986) *Agric. Biol. Chem.* **50**, 813.
32. Kashman, Y. and Carmely, S. (1980) *Tetrahedron Letters* **21**, 4939.
33. Rei, M. -H. (1978) *J. Org. Chem.* **43**, 2173.
34. Cheung, H. T. A., Brown, L., Boutagy, J. and Thomas, R. (1981) *J. Chem. Soc., Perkin Trans. I* 1773.
35. Bockbrader, H. N. and Reuning, R. H. (1983) *J. Pharm. Sci.* **72**, 271.
36. Bishara, R. H. and Schiff Jr., P. L. (1970) *Lloydia* **33**, 477.
37. Shoolery, J. N., Pradham, B. P. and Hassan, A. (1983) *Indian J. Chem.* **22B**, 727.
38. Birch, A. J., Collins, D. J., Muhammad, S. and Turnbull, J. P. (1963) *J. Chem. Soc.* 2762.
39. Kumar, V., Niyaz, N. M. M., Wickramaratne, D. B. M. and Balasubramaniam, S. (1991) *Phytochemistry* **30**, 1231.
40. Stahl, E. and Kaltenbach, U. (1961) *J. Chromatogr.* **5**, 351.
41. Piancatelli, G., Scettri, A. and D'Auria, M. (1982) *Synthesis* 245.
42. Saiki, Y., Fukuyama, E. and Tsuneya, T. (1987) *Yakugaku Zasshi* **107**, 219; *Chem. Abstr.* **106**, 211005a (1987).
43. Demole, E. and Enggist, P. (1983) *Helv. Chim. Acta* **66**, 1381.
44. Huffman, J. W., Swain, W. E., Jacobus, J. and McPhail, A. T. (1980) *J. Org. Chem.* **45**, 3088.
45. Schwartz, M. A. and Willbrand, A. M. (1985) *J. Org. Chem.* **50**, 1359.
46. Davies, N. W., Miller, J. M., Naidu, R. and Sotheeswaran, S. (1992) *Phytochemistry* **31**, 159.