DIMERIC ANTHRANOIDS FROM THE LEAVES OF *SENNA MULTIGLANDULOSA* AND *SENNA SEPTEMTRIONALIS*

BY

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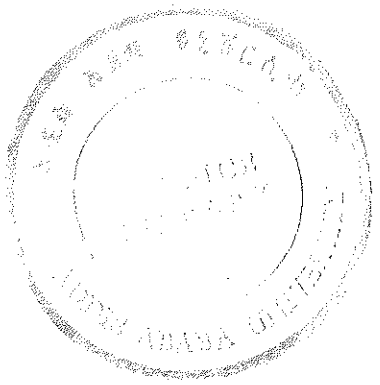

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE MASTER OF SCIENCE IN CHEMISTRY IN THE ADDIS ABABA UNIVERSITY

JUNE, 1990.

ACKNOWLEDGEMENTS

First and for most I would like to express my appreciation to my research adviser, Dr. Berhanu Abegaz for his constant guidance and supervision. I would also like to thank Dr. Gizachew Alemayehu, who shared his experience on the work. Dr. Thomas Gedris of The Florida State University is acknowledged for running high resolution NMR. I am indebted to academic, technical and research staff of the Department of Chemistry, fellow graduate students and friends for all their help and encouragements in the course of my study and research work.

Financial support from the Swedish Agency for Research Cooperation with Developing Countries (SAREC) which was used to cover partly the expenses incurred in the research work is gratefully acknowledged.

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ABSTRACT

DIMERIC ANTHRANOIDS FROM THE LEAVES OF *SENNA MULTIGLANDULOSA* and *SENNA SEPTEMTRIONALIS*

Senna multiglandulosa and *Senna septemtrionalis* are two of the eighteen *Senna* species found in Ethiopia.

The chloroform extract of *S. multiglandulosa* leaves, after repeated chromatography, have yielded four dimeric anthranoids. Three of these were identified to be anhydrophlegmacin-9,10-quinone (61), floribundone-1 (64), and torosanin-9,10-quinone (93). The structure of T-55-2, a fourth compound was partially established.

From the leaves of *S. septemtrionalis*, the two dimeric compounds, anhydrophlegmacin-9,10-quinone (61) and torosanin-9,10-quinone (93) were isolated.

To our knowledge Torosanin-9,10-quinone is reported here as a natural product for the first time, and there is only one report on the isolation of anhydrophlegmacin-9,10- quinone from higher plants. Floribundone-1 was isolated earlier from both plants.

1 INTRODUCTION

1.1 General

Plants have been utilized since thousands of years as sources of medicinals, spices, dyes, poisons, etc. The chemical compounds responsible for these activities are often the secondary metabolites of plants or natural products as they are usually referred to.

Natural products are still untapped reservoir of folkloric medicines. Especially in the developing countries they are well known substitutes to modern drugs which may be unavailable or unaffordable. It is also important to note that about 40% of modern drugs are of natural origin [1].

The study of natural products is a multidisciplinary activity embracing chemistry and a number of areas in biological sciences. Natural product chemistry involves isolation, characterization and the synthesis of compounds of natural origin.

Except for some speculations [2,3] the function of secondary

metabolites in plants is not well defined. On the other hand the study of structural inter-relationships, distributions and biogenetic origins of natural products is the basis of chemotaxonomy.

1.2 *Senna* species

The genus *Senna* in the Leguminosae family is known to have about 240 species distributed throughout the tropics and sub-tropics [4]. *Senna* species have received a lot of attention on account of their medicinal properties. They are mostly used in the treatment of skin diseases and are sources of the well known senna purgatives. Further applications of *Senna* species in traditional medicine are well documented in the literature [5-10].

1.3 Ethiopian *Senna* species

Ethiopian plant species which were belonging to the genus *Cassia* [11], according to a recent survey of the flora of Ethiopia, are regrouped into three genera namely: *Cassia*, *Senna* and *Chamecrista*. Accordingly, the new genus *Senna*

contains the following eighteen species. Synonyms are indicated in brackets. *Senna petersiana* (*Cassia petersiana*), *S. septemtrionalis* (*C. septemtrionalis*, *C. laevigata*, *C. floribunda*), *S. singueana* (*C. singueana*, *C. sabak*, *C. goratensis*), *S. baccarinii* (*C. baccarinii*), *S. occidenatlis* (*C. occidentalis*), *S. sophera* (*C. sophera*), *S.obtusifolia* (*C. obtusifolia*, *C. tora*), *S. siamea* (*C. siamea*), *S. didymobotrya* (*C. didymobotrya*), *S. ruspolii* (*C. ruspolii*), *S. longiracemosa* (*C. longiracemosa*), *S. ellisiae* (*C. ellisiae*), *S. truncata* (*C. truncata*), *S. italica* (*C. italica*), *S. holosericea* (*C. holosericea*), *S. multiglandulosa* (*C. multiglandulosa*, *S.tomentosa*, *C. tomentosa*) *S. alexandriana* (*C. alexandriana*, *C. senna*, *C. angustifolia*), *S. bicapsularis* (*C. bicapsularis*).

1.4 Objective of the study

The biological activities of *Senna* species are mostly believed to be due to anthranoids. Hence, the objective of this work is to extend further, earlier studies [12-14], dealing with the isolation and characterization of anthracene derivatives, which may have pharmacological as well as

chemotaxonomic values. The plants considered in this study are *S. septemtrionalis* and *S. multiglandulosa*.

Senna septemtrionalis is a woody herb, shrub or small tree 1 - 5 m high, distributed between altitudes of 1700 and 2400 m. In Ethiopia it is found in Arsi, Hararge, Illubabor, Kefa, Sidamo and Shewa regions. *S. multiglandulosa* is an ornamental shrub or tree, cultivated in Wolega, Shewa and Sidamo regions.

1.5 Anthraquinones and related compounds

1.5.1 Occurrence and distribution

Anthraquinones are by far the largest group of the natural quinones. They have been isolated from fungi, lichens bacteria, as well as some species of insects. Anthraquinones and related compounds in higher plants, are located in almost every part of the plant including root, heart wood, bark, leaves, seeds, and often occur as glycosides [15]. In the Leguminosae family, anthraquinones appear to be confined mostly to few genera. Anthraquinones of the Leguminosae are

listed in Appendix 1. The other anthranoids known to occur in the family, include anthrones (Appendix 2), pre-anthraquinones (Appendix 3), compounds formed by the union of two monomer units of anthracene derivatives (Appendix 4) and glycosides (Appendix 5).

1.5.2 Biological activities

Anthraquinones and their derivatives have been implicated as the purgative principles of senna. Chathartic action increases in the order anthraquinone, anthrone, bianthrone. Glycosides are more effective than aglycones in their purgative action. Many also claim [16], that both free anthraquinones and their glycosides are pharmacologically inactive and the pharmacologically important compounds are anthranols. The latter are believed to arise from the reduction of anthraquinones by intestinal micro flora [17]. Other biological activities of anthraquinones include antiviral [18,19], antihelmintic [20] and antifungal [21] properties.

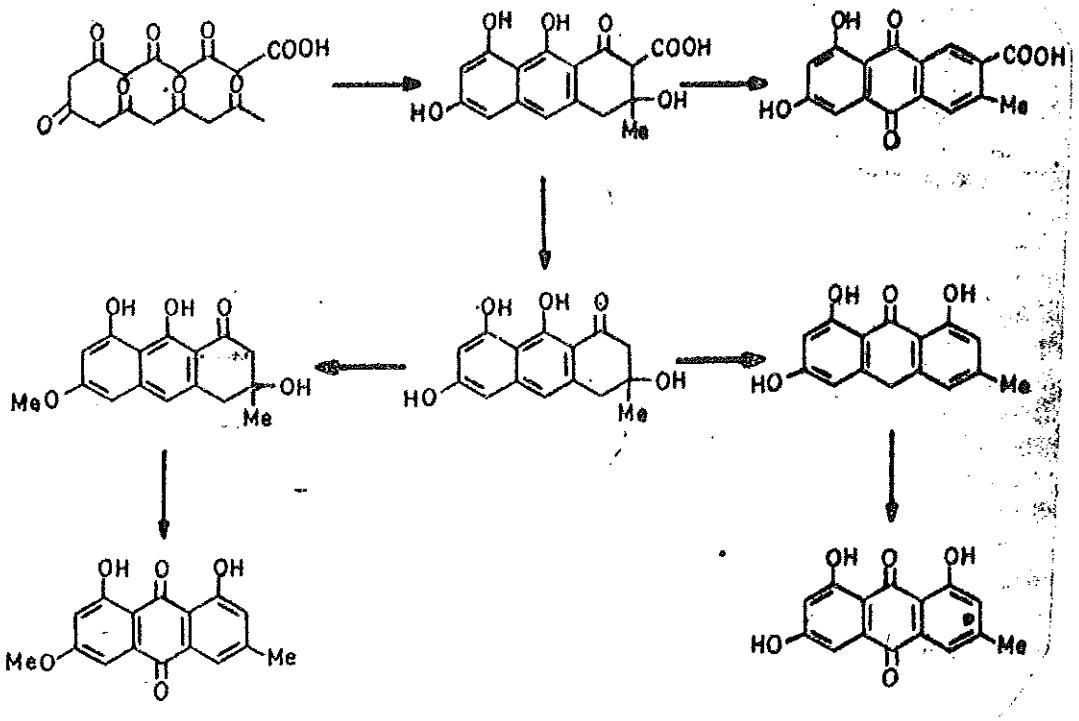
1.5.3 Biogenetic relationship

Generally, the biosynthesis of anthraquinones is believed to follow two routes, the acetate-malonate pathway and the shikimate-mevalonate pathway [22]. Based on their structure and biosynthesis, anthraquinones are classified into either the emodin-type or the alizarin-type. Those anthraquinones with substituents on both benzenoid rings, follow the acetate-malonate biogenetic route, and are of the emodin type. Anthraquinones of the alizarin-type are totally devoid of substituents on one benzenoid ring and they arise by the shikimate-mevalonate pathway.

Anthraquinones of the Leguminosae have substituents on both rings with the exception of rubiadin (10) and domnacanthal (11). The most plausible biogenetic route for anthraquinones in the Leguminosae, therefore, appears to be of the polyketide origin. This is supported by labelling experiment [23], which showed that, in higher plants, the biosynthesis of the emodin type anthraquinones proceed *via* the poly acetate pathway.

In lower plants the biogenetic relationship of anthraquinones and related compounds is proposed [24,25] to be as shown in Scheme I.

The co-occurrence [26,27], of torosachrysone (47), physcion (3) and physcion anthrone (46) with phlegmacins (60), anhydrophlegmacin(62) anhydrophlegmacin-9,10-quinone (61) and torosanin (63) in *C. torosa* suggests that, similar biogenetic route, which involves the conversion of pre-anthraquinones to anthraquinones may be followed in higher plants too.



Scheme I Biogentic relationship of anthranoids

Experimental evidence indicated [26] that, in the seedlings of *C. torosa*, germichrysone (50) is not derived from anthraquinone, but it is a product of *de novo* biosynthesis. Thus, it is possible to infer that, in plants the reduction of anthraquinones to pre-anthraquinones is least likely to occur.

Anthraquinones of the emodin type take their start at carbon-oxygen skeleton generated from joining of acetate units, in head-to-tail linkage, which then undergo subsequent structural modifications. These modifications may be principally the introduction and removal of oxygen, alkylation (notably with methyl), glycosidation, and dimerization.

1.5.4 Identification of Anthranoids

i. Color reactions

Color reactions are useful particularly at the beginning of an investigation where crude extract or even tissues may yield information of value. The maceration of powdered plant

material with organic solvents followed by filtration and addition of aqueous ammonia or sodium hydroxide, leads to the formation of pink, red or violet color, if hydroxy anthraquinones are present [28]. This test is general for all quinones with free hydroxyl groups.

The orientation of hydroxyl groups of hydroxy anthraquinones can also be predicted by the color change observed in alkaline solution or when they are treated with methanolic magnesium acetate [29].

ii. Ultraviolet-visible spectra

The spectra of anthraquinones is dominated by the influence of hydroxyl substituents. The absorption spectrum of anthraquinones consists of intense benzenoid absorption at 240 - 290 nm, medium absorption at 320 - 330 nm, and a strong quinonoid absorption at 405 nm. These areas of absorption are characteristic and the pattern in the ultraviolet region is not seriously affected by substitution.

Several surveys of the ultraviolet-visible spectra which may

help in structure determination of anthraquinones are documented in the literature [30-33].

iii. Infrared spectra

The carbonyl frequency of anthraquinones are useful diagnostic aids in structrue determination. The carbonyl absorption of 9,10-anthraquinones with no α-hydroxyl group falls at around 1678 cm^{-1}. Hydrogen bonding, substitution either in the quinonoid or an adjacent benzenoid ring with +I or +M groups and separation of the carbonyl function so that the quinonoid conjugation extends through more than one ring results in lower frequency. A second carbonyl band at lower frequency can be observed if the anthraquinone contains a hydroxyl group in the α- position due to chelation and conjugation. The results of Bloom and co-workers [34] can also be used for correlation between the carbonyl frequency range and the α-hydroxyl groups.

Anthraquinones with one hydroxyl group in the β-position on the nucleus or attached to a substituent group have one

hydroxyl stretching band. The appearance of more than one hydroxyl band between 3600 cm^{-1} and 3150 cm^{-1} indicates more than one such hydroxyl group.

iv. Proton magnetic resonance spectra

In 9,10-anthraquinone the α- and β-protons give multiplets centered at 8.07 and 7.67 ppm, respectively and are modified by substitution. Hydroxyl groups at positions 1, 4, 5 and 8 are easily distinguished by their appearance at unusually low field resonance between 11 and 14 ppm, a shift accounted for by the chelation of hydroxyl groups with 9,10-keto groups.

Information about orientation of substituents around the aromatic ring system can be obtained from the chemical shift positions of aromatic protons. In this connection, since many quinones are phenolic, calculation of theoretical chemical shifts by the use of shielding parameters compiled [35] for phenolic compounds can be used to predict the chemical shift of the aromatic protons and hence orientation of substituents.

Splitting patterns and coupling constants have also diagnostic value for the determination of orientation of substituents. *Ortho* coupling constant (*Jo*) is usually around 7 - 9 Hz, *meta* coupling constant (*Jm*) is 2 - 3 Hz and *para* coupling constant (*Jp*) is *ca.* 1 Hz. Zanger [36] has pointed out that any single aromatic proton may exhibit only one of the seven possible first order splitting patterns. Of these, anthraquinones of the chrysophanol type show *ortho-meta* (doublet of doublet) and di-*ortho* (broad triplet) pattern for the protons at positions 5 or 7 and 6, respectively. Emodin or physcion type anthraquinones have simpler spectra and show *meta* (narrow doublet) multiplicity pattern.

2.1 *Senna multiglandulosa* leaves

2.1.1 General

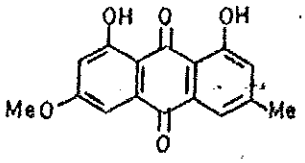
There are two conflicting chemical reports on *S. multiglandulosa*. One of these claims the absence of hydroxy anthraquinones [37], while the other describes [13] the isolation of floribundone-1 (64), a hydroxy bi-anthraquinone.

Our investigation of the chloroform extract of the leaves of *S. multiglandulosa*, after repeated chromatography, (see Experimental) has resulted in the isolation of four dimeric anthracene derivatives, T-55-1, T-55-2, T-55-3 and T-55-4. T-55-1 is characterized to be floribundone-1 (64), isolated earlier from the same plant [13]. T-55-3 is found to be anhydrophlegmacin-9,10-quinone (61). This is the second report of this pigment from higher plants. The molecular structure of T-55-4 is identified to be 7,5'-physcion-torosachrysone (93). Early workers [38] have obtained this

compound as oxidation product and named it torosanin-9,10-quinone(93). This is the first report of torosanin-9,10-quinone as a natural product. The structure of T-55-2 is established partially. Its small quantity (2 mg) hindered complete structure elucidation.

2.1.2 Torosanin-9,10-quinone (93)

Compound 93, a dark red pigment, had an R_f value of 0.50 (Silica gel, $CHCl_3$/MeOH, 100:1). It showed a color change from yellow to pink when the TLC plate was sprayed with ethanolic KOH (5%). This is a characteristic color change for hydroxy anthraquinones. The IR spectrum showed



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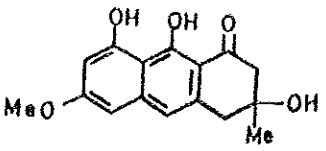

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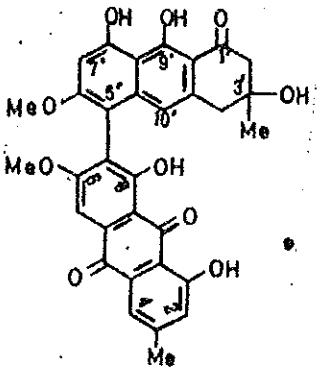


93

absorption bands due to a hydroxyl group (3400 cm^{-1}), a non-chelated carbonyl group (1670 cm^{-1}) and a chelated carbonyl group (1640 cm^{-1}). The UV spectrum absorption maxima at 235, 278 and 407 nm suggested a quinonoid chromophore in 93.

The ^{1}H NMR spectrum of 93 revealed the presence of the following groups: four chelated and one non-chelated hydroxyl groups, five aromatic protons, two methoxyl groups, one aromatic methyl, one non-aromatic methyl and two methylene groups. A monomeric anthranoid unit could not accommodate all the above substituents, and hence, this compound is proposed to be a dimer.

The chemical shifts of 93 were suggestive of the presence of physcion (3) and torosachrysone (47) moieties (Table 1). This was further established by alkaline sodium dithionite cleavage of 93 which produced physcion. The CIMS of 93 showed a base peak at *m/z* 553, presumably as a result of loss of water from the molecular ion. Comparison of the ^{1}H NMR of 93 with that of 47 revealed that, the signal in the spectrum of 93 due to H-7' was shifted downfield by 0.3 ppm and the

signal of H-10' was shifted upfield by 0.54 ppm as compared to the corresponding signals in 47. The signal for H-5' on 47 had disappeared in the spectrum of 93. Thus the physcion moiety is linked to C-5' of the torosachrysone moiety. The chemical shifts of the physcion moiety of 93 closely resemble those of physcion except for the absence of the signal attributed to H-7. This suggested a linkage between the two monomeric units at C-5' of the torosachrysone and C-7 of the physcion moieties.

Base treatment of 93 (see Experimental) yielded 7,5'-biphyscion (64), which was identical to an authentic sample of 64 by co-TLC comparison. This supports the proposed 7,5'-coupling of the monomeric units in 93.

Table 1 ^{1}H NMR data of 3*, 47* (100 MHz, $CDCl_3$), 61 and 93 (270 MHz, $CDCl_3$, δvalues)

Assignment	3	47	61	93
2-H	7.04		7.12	7.11
3-Me	2.45		2.49	2.48
4-H	7.57		7.69	7.68
5-H	7.32		7.58	7.58
6-OMe	3.92		3.71	3.89
7-H	6.60		-	-
8-OH	12.05		12.01	12.10
1-OH	12.26		12.42	12.34
2'-CH_2-		2.80	2.72	2.81
3'-Me		1.30	1.35	1.38
3'-OH		2.00	-	1.55
4'-CH_2-		2.98	2.85*q*	2.92
			J=18	
5'-H		6.60	6.07	-
6'-OMe		3.84	3.89	3.83
7'-H		6.40	6.53	6.70
8'-OH		9.87	10.23	10.26
9'-OH		15.88	16.72	16.41
10'-H		6.95	-	6.41

* Taken from ref. [38]

Floribundone-1 (64), was isolated from the leaves of *S. multiglandulosa* and *S. septemtrionalis* by Alemayehu *et al.* [13,14]. From the co-occurrence of 64 and 93, it can be presumed that 93 is a biogenetic precursor, which upon biological oxidation is converted to 64. 93 is optically active with a specific rotation, $[\alpha]_D^{22} = +60^\circ$.

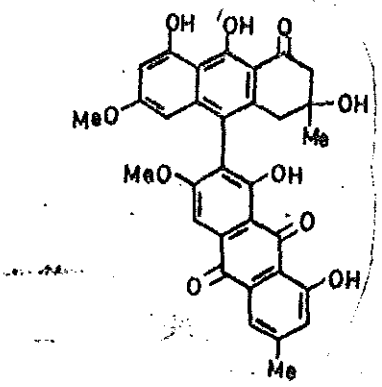
Kitanaka *et al.* [38] reported the first 7,5'- linked dimeric anthracene derivative, torosanin (63), which was isolated from *Cassia torosa*. Oxidation of torosanin resulted in the formation of torosanin-9,10-quinone, for which structure 93 was assigned. Spectroscopic data reported for torosanin-9,10-quinone closely agree with that generated for 93. This is the first report of torosanin-9,10-quinone (93) as a natural product.

2.1.3 Anhydrophlegmacin-9,10-quinone (61)

Compound 61, a dark red pigment, had an R_f value 0.51 (Silica gel, $CHCl_3$/MeOH, 100:1). It gave a positive color reaction for hydroxy anthraquinone. The UV spectrum had absorption maxima at 236, 273 and 409 nm. The IR spectrum showed

absorption bands at 3400, 1660, and 1630 cm^{-1}, caused by a hydroxyl, a non-chelated quinonoid carbonyl and a chelated carbonyl groups, respectively.

Structure 61 was assigned to this compound based mainly on the following ^{1}H NMR evidences. The singlets at 16.72 and 10.23 ppm indicate the presence of a pre-anthraquinone moiety. The former signal is attributable to a doubly chelated C-9 hydroxyl group and the latter to a phenolic C-8 hydroxyl group.



61

The aromatic region displayed five aromatic proton resonances at 7.61, 7.58, 7.12, 6.53 and 6.07 ppm. In addition to these, the presence of one aromatic methyl group (δ2.49),an aliphatic methyl group (δ1.35), two methylene groups (δ2.72

and 2.85) and two methoxyl groups(δ3.89 and 3.71) were also evident from the ^{1}H NMR spectrum. As in compound 93, the above discussed ^{1}H NMR spectrum clearly suggests that, compound 61 also to be a dimeric molecule. A close comparison of the ^{1}H NMR chemical shifts of 3 and 47 with that of 61 led to the identification of physcion (3) and torosachrysone (47) as the monomeric units. The presence of these two moieties was further supported by the alkaline sodium dithionite cleavage of 61, which yielded physcion (3). The proton decoupled ^{13}C NMR spectrum indicated 32 carbon resonances out of which 7 appeared below 71 and 25 above 99 ppm (Table 2) in consistence with the proposed structure 61. The CIMS of 61 also showed a molecular ion peak at *m/z* 571 in good agreement with the presence of the two moieties.

Table 2 ^{13}CMR data* for 61 ($CDCl_3$, 75 MHz).

C	δvalue	C	δvalue
1'	202.5	1	161.38
2'	50.39	2	125.11
3'	70.52	3	135.52
3'-Me	28.85	3-Me	22.09
4'	41.4	4	121.79
4a'	139.92	4a	134.41
5'	99.57	5	103.62
6'	167.82	6	164.64
6'-OMe	56.61	6-OMe	55.34
7'	100.16	7	111.48
8'	164.25	8	163.08
8a'	108.17	8a	108.33
9'	161.90	9	191.64
9a'	120.48	9a	113.80
10'	118.63	10	182.49
10a'	149.22	10a	135.52

* The assignment was done by comparison with reported data [25]

Furthermore, the ^{1}H NMR of 61 revealed a meta coupling pattern between the signals at 6.07 and 6.53 ppm attributable to H-5' and H-7' of the torosachrysone moiety, respectively. This ruled out the possibility of C-5' and C-7' as coupling positions. Besides, the absence of an aromatic proton signal assignable to H-10' established C-10' of the torosachrysone moiety as the linkage point. The signals at 7.12, 7.69 and 7.58 ppm are assignable to H-2, H-4 and H-5 of the physcion moiety, respectively. In the physcion moiety, therefore, the only possible coupling position is C-7.

The signals for H-4' and H-5' of the torosachrysone moiety are upfield shifted by 0.13 and 0.53 ppm relative to the corresponding signals in torosachrysone, respectively. A possible cause for this upfield shift may be the conformation of the dimer which would result in the shielding of these protons by the physcion moiety. Another interesting observation realized from the ^{1}H NMR spectrum of 61 was that, the C-2' methylene protons signal at 2.72 ppm appeared as a singlet while the C-4' methylene protons signal appeared as a quartet centered at 2.85 ppm with a geminal coupling constant of 18 Hz. The above presented spectroscopic argument allows

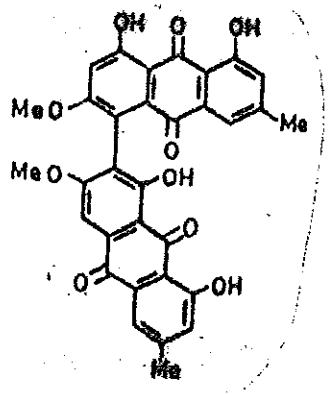
the identification of this compound as anhydrophlegmacin-9,10-quinone(61).

Two pairs of dimeric anthracene derivatives possessing similar structure are known. One pair was isolated from higher fungus [57], and are the (-)-stereoisomers. Their enantiomers, the (+)-stereoisomers, were reported [27] from *Cassia torosa*. The specific rotation of 61, $[\alpha]_D^{22} = +40^o$. This supports the idea of Takhashi *et al.* [27] who proposed that, the biosynthesis of the monomeric unit torosachrysone (47) proceeds stereospecifically to produce (+)-torosachrysone in higher plants and (-)-torosachrysone in the fungus.

2.1.4 Floribundone-1 (64)

The positive color change using ethanolic KOH (5%) coupled with the UV absorption maxima at 443, 360, 276 and 236 nm suggested an anthraquinone chromophore. The ^{1}H NMR spectrum of this compound revealed the presence of four chelated hydroxyl groups, six aromatic protons, two methoxyl groups and two aromatic methyls suggesting a bianthraquinone structure. T-55-1 and physcion (3) have similar ^{1}H NMR

spectra. The difference between the spectrum of T-55-1 and that of physcion is the presence of two singlets at δ7.57 and 6.83 in the spectrum of T-55-1, whereas the corresponding signals in the spectrum of physcion appear as doublets at δ7.32 and 6.60 (J = 2.5 Hz). The latter signals represent the H-5 and H-7 of physcion, respectively. This is



64

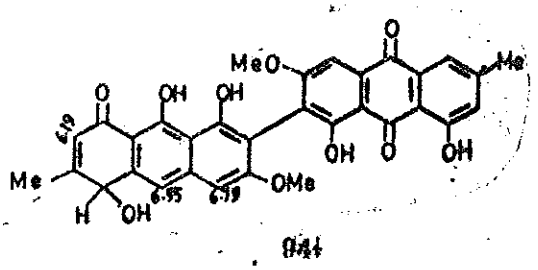
consistent with a 5,7'- coupled biphyscion. Spectroscopic data as well as direct comparison with an authentic sample showed that T-55-1 is floribundone-1 (64), isolated from the same plant [13]. The chemical shifts for the protons of T-55-1 were assigned using the data for physcion [27] and floribundone-1 [14].

2.1.5 Compound T-55-2

The UV spectrum of this compound had absorption maxima at 243, 272 and 468 nm suggesting a quinonoid chromophore. The proton resonance signals at 17.25 and 10.37 ppm, could be assigned to a doubly chelated and a phenolic hydroxyl groups, respectively. The aromatic region of the ^{1}H NMR spectrum displayed six proton signals out of which three at 7.10, 7.69 and 7.58 ppm are assignable to H-2, H-4 and H-5 of a physcion moiety, respectively. The remaining three aromatic signals suggest the presence of another aromatic group.

The CIMS of compound T-55-2 had a base peak at *m/z* 569. Based on these spectroscopic data three possible structures 94, 95 and 96 are proposed. Structure 95 has molecular weight 566, which did not appear in the MS or could not rationalized by any of the ion peaks. Moreover the chemical shift position at 6.79 ppm is downfield than expected for such a proton. The hydroxyl signal at 17.25 ppm suggests torachryosne (97) like structure. Structure 96 has this group. But, its molecular weight 514, although appears in the MS, its relation to the major ion peaks could not be

accounted for. Biogenetic consideration of 96 also suggests a methyl group at the linkage position of the torachrysone like part, which is not possible in 96. The molecular weight of 94, 568, agrees with the base peak in the CIMS, which appeared at *m/z* 569. All protons have signals in the ^{1}H NMR spectrum, except for one proton at C-4', which is expected to appear *Cα*. 4.3-4.6 ppm.



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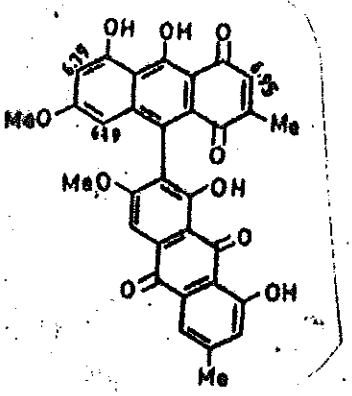

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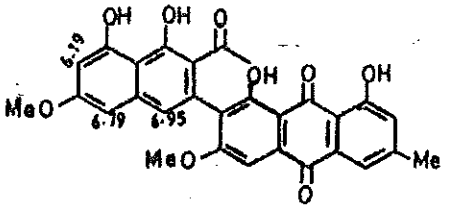
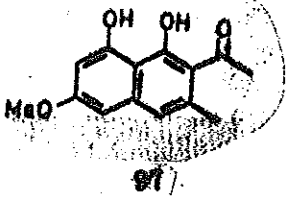


96



97

2.2 *Senna septemtrionalis* leaves

2.2.1 General

Chemical reports in the literature indicate the pods, roots and seeds of *S. septemtrionalis* have yielded 8-mono- and di-galactosides of physcion as well as chrysophanol and emodin [40-42]. Flavonoids including ombuin and quercetin have been reported from the roots, leaves and seeds [43-45]. In addition, the isolation of N^1,N^8-dibenzoylspermidine, and the dimeric anthracene derivatives floribundone-1 (64) and floribundone-2 (65) from the leaves, have also been reported [14]. In this study, the chloroform extract of the leaves of *S. septemtrionalis* was chromatographed to result in two pigments, S-32-2a and S-33-1 (see Experimental). The structure of S-32-2a was established to be 93 and that of S-33-1 was identified as 61.

2.2.2 Compound S-32-2a(93)

The molecular ion peak in the EIMS of this compound appeared at *m/z* 570 and the base peak was at *m/z* 552 as a result of

loss of water from the molecular ion. The UV spectrum had absorption maxima at 421, 281 and 231 nm suggesting an anthraquinone chromophore. The ^{1}H NMR spectrum showed signals for two methyl groups, two groups of methylene protons and two methoxyl groups. The aromatic region displayed three signals at 7.7, 7.6 and 7.1 ppm, assignable to a physcion moiety. The other two signals in the aromatic region at 6.7 and 6.4 ppm were indicative of a torosachrysone moiety. A close analysis of the ^{1}H NMR spectrum showed S-32-2a to be a dimer of 3 and 47. In the ^{1}H NMR spectrum there are no signal assignable to H-7 of the physcion part and H-5' of the torosachrysone moiety, thereby establishing the 7,5'-linkage of the two monomeric units. Color reactions as well as spectroscopic data (see Experimental) of S-32-2a were similar to those obtained for compound 93. Hence, the structure of this compound is established to be 93.

2.2.3 Compound S-33-1 (61)

The presence of anthraquinone chromophore, in this compound was evident from the UV absorption maxima at 411, 277 and 236 nm. In the ^{1}H NMR spectrum a doubly chelated hydroxyl group

(16.7ppm) and a phenolic hydroxyl group (10.3 ppm) were indicative of a pre-anthraquinone like skeleton. Signals at 12.0 and 12.4 ppm were suggesting hydroxyl groups *peri*- to a carbonyl. The ^{1}H NMR spectrum also showed proton resonance signals due to two methyls, two methylenes, and two methoxyls. The aromatic region of the spectrum, when expanded, displayed five aromatic protons. The signals at 6.04 and 6.49 ppm are doublets with a meta coupling constant, J = 2.2 Hz. Hence, the signals at 6.04 and 6.49 ppm are assignable to H-5' and H-7' of a torosachrsone moiety, respectively. The presence of a physcion moiety was also derived from the proton resonance signals at 7.08 7.68 and 7.55ppm, attributable to H-2, H-4 and H-5, respectively. The EIMS of this compound had a molecular ion peak at *m/z* 570 confirming the presence of the two monomeric units. In the ^{1}H NMR spectrum, signals assignable to H-10' and H-7 were not displayed. This establishes the structure of S-33-1 to be 61. This was confirmed by close comparison of spectra of S-33-1 with those acquired for 61 (see Experimental).

3.1 General

Instruments. Melting points were determined by Kofler block hot stage melting point apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer 727 B Spectrophotometer. Milton Roy Spectronic 1001 instrument was used to record the UV absorption maxima. Optical rotation were measured on Perkin-Elmer 241 polarimeter. ^{1}HNMR data were obtained using Bruker 270 MHz. ^{13}CNMR spectrum was acquired on Bruker 75 MHz instrument.

Chromatography. Analytical TLC were performed using silica gel (Merk) coated on aluminium foil (0.25 mm thickness). Preparative TLC were run on silica gel (Merk) precoated glass plates with 0.25 mm thickness. For column chromatography and Vacuum Liquid Chromatography (VLC), silica gel (Merk) impregnated with 0.5 N oxalic acid was used.

3.2 *Senna multiglandulosa* leaves

Plant material. *Senna multiglandulosa* leaves were collected on the road from Addis to Ambo in December 1990. Voucher specimen (MB-2) is deposited in the National Herbarium, Addis Ababa University.

Extraction and isolation. 400 g leaves were dried and powdered. The ground leaves were then soaked in 5% acetic acid (1.5 l) for 24 hrs. After drying the acetic acid treated leaves were defatted with petrol (5 l). The marc was then extracted with chloroform (10 l). The solvent was removed to yield 15 g extract. The chloroform extract was applied on VLC, eluted with petrol/EtOAC (19:1) (5 l) and chloroform (5 l), successively. The chloroform extract 2.5 g black semi solid, showed more than four anthranoids on TLC. Its separation on Sephadex LH-20 (MeOH/$CHCl_3$, 1:1) resulted in three fractions. The first fraction contained only green pigments and was discarded. The third fraction showed one major yellow spot which was identified to be emodin by TLC comparison. The second fraction had the four major and other

trace anthranoids. Preparative TLC, eluted with $CHCl_3$/MeOH (100:2) of this fraction yielded four pigments, 61, 64, 93 and T-55-2.

3.3 Characterization of the pigments of *Senna multiglandulosa*

Anhydrophlegmacin-9,10-quinone (61). Dark red pigment, mp. 187-189° (Lit [27] 192-3°)UV $\lambda_{max}^{CHCl_3}$ nm (logε): 409(4.21), 306(4.21), 273(4.76), 236(4.97); IR ν_{max}^{KBR} cm^{-1}: 3400, 2960, 1675(sh), 1630, 1610, 1280, 1220, 1170, 1150; ^1H NMR: See Table 1; ^{13}C NMR: See Table 2 CIMS (*iso*-butane) *m/z* (rel.int.): 571 $[M+H]^+$ (13), 553 $[M+H-H_2O]^+$ (100), 539 $[M+H-OMe]^+$ (29), 285 $[M+H-286]^+$ (24), 271 (47); Optical rotation: $[\alpha]_D^{22}$ + 40° ($CHCl_3$, c = 0.001).

Reductive cleavage of 61. To a solution of 61 (2 mg) in 2 ml aqueous NaOH (5%), sodium dithionite (10 mg) was added and left for 24 hrs. The solution was then acidified and extracted with $CHCl_3$, dried and chromatographed on micro column (Si gel, Benzene/ EtOAc 19:1) to give physcion.

Torosanin-9,10-quinone (93). Dark red pigment; mp. 222-5° (Lit.[38] 230-3°); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 407(3.84), 330(3.35), 305(3.84), 278 (4.32), 236(4.88); IR ν_{max}^{KBR} cm^{-1}: 3450, 2950, 1675(sh), 1640, 1480, 1400, 1340, 1280, 1220, 1120; ^1H NMR: See Table 1; CIMS(*iso*-butane) *m/z* (rel. int): 553 $[M+H-H_2O]$ (100), 539 $[M+H-OMe]^+$ (65), 299 $[M+H-270]^+$(6) 285 $[M+H-286]^+$ (13), 271 (17); optical rotation: $[\alpha_D^{22}]$ + 60° ($CHCl_3$, c = 0.001).

Reductive cleavage of 93. The same procedure as in 61 resulted in physcion

Oxidation of 93. 5 mg of 93 was dissolved in 5% NaOH and left for 24 hrs. The solution was then acidified and extracted with CH_2Cl_2. After the solvent has been removed the resulting extract was chromatographed on a micro column (Si. gel, Benzene/EtOAc, 19:1) to yield floribundone-1 (64).

Floribundone-1 (64). Orange pigment; mp. 290-300° (Lit [14] >260); UV $\lambda_{max}^{CHCl_3}$ nm (logε): 443 (4.27), 360 (4.05), 276 (4.54), 236 (4.96); ^1H NMR (270 MHz, $CDCl_3$): δ2.35 (3H, *s*, 3-Me), 2.47 (3H, *s*, 3'-Me), 3.83 (3H, *s*, -OMe), 3.88 (3H, *s*,

-OMe), 6.81 (1H, *s*, 7-H), 7.05 (1H, *s*, 2-H), 7.08 (1H, *s*, 2'-H), 7.41 (1H, *s*, 4-H), 7.55 (1H, *s*, 5'-H), 7.67 (1H, *s*, 4'-H), 12.06 (1H, *s*, 8-OH), 12.12 (1H, *s*, 1-OH), 12.20 (1H, *s*, 1'-OH), 13.04 (1H, *s*, 8'-OH).

Compound-T-55-2. Dark brown pigment; mp. 188-192°; UV $\lambda_{max}^{CHCl_3}$ nm: 480, 310(sh), 272, 250, 243; ^{1}H NMR (270 MHz, $CDCl_3$): δ2.34 (3H,*s*), 2.49 (3H,*s*), 3.83 (3H,*s*), 3.86 (?,*s*), 6.19 (1H, *s*), 6.79 (1H, *s*), 6.95 (1H, *s*), 7.10 (1H, *s*), 7.59 (1H, *s*), 7.69 (1H,*s*), 10.37 (1H,*s*), 12.04 (1H, *s*), 12.25 (1H, *s*), 17.25 (1H, *s*); CIMS (*iso*-butane) *m/z* (rel. int.): 569 (100), 285 (73), 271 (26).

3.4 *Senna septemtrionalis* leaves

Plant material. Senna septemtrionalis leaves were collected from the experimental garden, Department of Chemistry, Addis Ababa University in February 1990. Voucher specimen (MB-1) is deposited in the National Herbarium, Addis Ababa University.

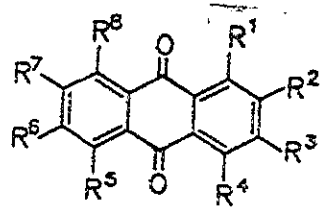
Extraction and isolation. The air dried and powdered leaves (300 g) were soaked in 5% acetic acid (1 l) for 24 hrs. and dried. The acetic acid treated leaves were defatted with petrol(7 l). After being defatted the marc was extracted using chloroform (10 l). The extract was concentrated to yield 20 g black waxy solid. The chloroform extract was filtered on VLC, eluted succesively with petrol/EtOAc, (19:1) and chloroform. The chloroform eluted fraction gave 15 g gummy material. Subsequent application of this material on column chromatography using chloroform as eluent could not result in good separation of the pigments. All fractions collected were combined and the resulting concentrate (10 g) was subjected to separation on Sephadex LH-20, eluted with $CHCl_3$/MeOH (1:1) to give three fractions. The first fraction showed no anthranoids and was discarded. The third fraction contained emodin. The second fraction contained two major and other trace anthranoids. This fraction applied on preparative TLC, eluted with $CHCl_3$/MeOH (100:2) resulted in the isolation of compounds 61 and 93

3.5 Characterization of the pigments of *Senna septemtrionalis*

Compound-S-32-2a (93). Dark red pigment; mp. 225-30°; UV $\lambda_{max}^{CHCl_3}$ nm (logε): 421 (4.18), 340 (3.68), 303 (4.17), 281 (4.64), 235 (4.95); ^{1}HNMR (270 MHz, $CDCl_3$): δ1.4 (3H, *s*, 3'-Me), 2.5 (3H, *s*, 3-Me), 2.8 (2H, *d* like, 4'-CH_2-), 2.9 (2H, *s*, 2'-CH_2-), 3.8 (3H, *s*, -OMe), 3.9 (3H, *s*, -OMe), 6.4 (1H, *s*, 10'-H), 6.7 (1H, *s*, 7'-H), 7.1 (1H, *s*, 2-H), 7.6 (1H, *s*, 5-H), 7.7 (1H, *s*, 4-H), 10.3 (1H, *s*, 8'-OH), 12.1 (1H, *s*, 8-OH), 12.3 (1H, *s*, 1-OH), 16.4 (1H, *s*, 9'-OH); EIMS 70 eV *m/z* (rel. int.): 570 $[M]^+$ (4), 552 $[M-H_2O]^+$ (100), 521 (15), 372 (77), 296 (31), 276 (23), 239 (23), 213 (27), 172 (31).

Compound S-33-1. Dark red pigment, mp. 185-7°; UV $\lambda_{max}^{CHCl_3}$ nm (logε): 411 (4.16), 307 (4.16), 277 (4.61), 236 (4.95); ^{1}HNMR (270 MHz, $CDCl_3$): δ1.4 (3H, *s*, 3'-Me), 2.5 (3H, *s*, 3-Me), 2.8 (2H, *s*, 2'-CH_2-), 2.9 (2H, *q*, J = 18 Hz, 4'-CH_2-), 6.04 (1H, *d*, J = 2.2 Hz, 5'-H), 6.49 (1H, *d*, J = 2.2 Hz, 7'-H), 7.1 (1H, *s*, 2-H), 7.6 (1H, *s*, 5-H), 7.7 (1H, *s*, 4-H), 10.2 (1H, *s*, 8'-OH), 12.0 (1H, *s*, 8-OH), 12.4 (1H, *s* ,1-OH), 16.7 (1H, *s*, 9'-OH); EIMS 70 eV *m/z* (rel.int): 570 $[M]^+$ (4), 552 $[M-H_2O]^+$ (100), 521 (15), 372 (77), 296 (31), 276 (23), 239 (23), 213 (27), 172 (31).

ndix 1 Anthraquinones of the Leguminosae

Name	Structure								Source *	Ref.
										
	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8		
Chrysophanol	OH	H	Me	H	H	H	H	OH	Cassia spp., Abrus contoniensis	[15,46]
Emodin	OH	H	Me	H	H	OH	H	OH	Cassia spp.	[15]
Physcion	OH	H	Me	H	H	OMe	H	OH	Cassia spp., Abrus cbntonieneis. Cajanus cajan. Desmodium pulchellum	[15,46
Aloe-emodin	OH	H	CH_2OH	H	H	H	H	OH	Cassia spp.	[15]
Rhein	OH	H	COOH	H	H	H	H	OH	Cassia spp.	[15,46
Obtusifolin	OMe	OH	Me	H	H	H	H	OH	C. obtusifolia	[47]
Aurantio-obtusin	OMe	OH	Me	H	H	OH	OMe	OH	C. obtusifolia	[47]
Obtusin	OMe	OH	Me	H	H	OMe	OMe	OH	C. obtusifolia	[47]
Chryso-obtusin	OMe	OH	Me	H	H	OMe	OMe	OMe	C. obtusifolia	[47]

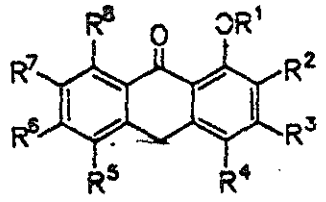
the Table C.= Cassia

Rubiadin	OH	Me	OH	H	H	H	H	H	C. multijuga	[46]
Damnacanthal	OMe	CHO	OH	H	H	H	H	H	Derris brevipes	[46]
Isochrysophanol	OH	Me	H	H	H	H	H	OH	C. afata	[46]
Chrysophanol 8-methyl ether	OH	H	Me	H	H	H	H	OMe	C. speciosa, C. multijuga C. obstrusifolia	[46]
8-Hydroxy rubiadin	OH	Me	OH	H	H	H	H	OH	C. alata, C. multijuga, C. spectobilis	[46]
Questin	OH	H	Me	H	H	OH	H	OMe	C. obtusifolia	[46]
Emodin 6,8-dimethyl-ether	OH	H	Me	H	H	OMe	H	OMe	Melanoxylon braunia	[46]
Citreorosein 6,8-dimethyl ether	OH	H	CH_2OH	H	H	OMe	H	OMe	Melanoxylon braunia	[46]
Islandicin	OH	H	Me	OH	H	H	H	OH	C. occidentalis	[46]
Helmihosporin	OH	H	Me	H	OH	H	H	OH	C. occidentalis	[46]
7-Hydroxyemodin-6. dimethyl ether	OH	H	Me	H	H	OMe	OH	OMe	Melanoxylon braunis	[46]
5-Hydrxyemodin	OH	H	Me	H	OH	OH	H	OH	C. javanica	[46]
Xanthorin	OH	H	Me	H	OH	OMe	H	OH	C. occidentalis, C. torosa, C. obtusifolia	[46.4
1.4.5-Trihydroxy-7-methoxy-3-methyl-anthraquinone	OH	H	Me	OH	OH	H	OMe	H	C. occidentalis	[46]
1.3.5-Trihydroxy-8-	OH	Me	OH	H	OH	H	H	OMe	C. alata	[46]

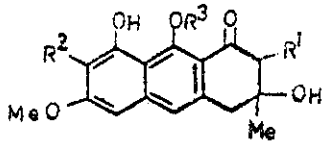
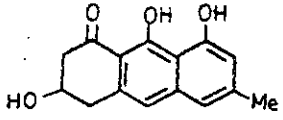
1,3,8-Trihydroxy-6-methoxy-2-methyl-anthraquinone	OH	Me	OH	H	H	OMe	H	OH	C. multijuga	[46]
1,8-Dihydroxy-3,6-dimethoxy-2-methyl-7-vinyl-anthraquinone	OH	Me	OMe	H	H	OMe	$CH=CH_2$	OH	C. sorbora	[46]
1,3-Dihydroxy-6,8-dimethoxy-2-methyl-anthraquinone	OH	Me	OH	H	H	OMe	H	OMe	C. multijuga	[46]
2,7-Dihydroxyemodin 8-methyl ether	OH	OH	Me	H	H	OH	OH	OMe	Melanorylon braunia	[46]
2,7-Dihydroxyemodin 6,8- dimethyl ether	OH	OH	Me	H	H	OMe	OH	OMe	C. sorbora	[49]
2,7-Dihydroxyemodin 7,8-dimethyl ether	OH	OH	Me	H	H	OH	OMe	OMe	C. sorbora	[50]
1-De-O-methylchryso-obtusin	OH	OH	Me	H	H	OMe	OMe	OMe	C. obtusifolia	[46]
1-De-O-methyl-obtusin	OH	OH	Me	H	H	OH	OMe	OMe	C. obtusifolia	[46]
1-De-O-methylaurantio-obtusin	OH	OH	Me	H	H	OH	OMe	CH	C. obtusifolia	[46]
1,3,5-Trihydroxy-6,7-dimethoxy-2-methyl-anthraquinone	OH	Me	OH	H	OH	OMe	OMe	OH	C. tora	[46]
1,8-Dihydroxy-3,5,7-trimethoxy-2-methyl-anthraquinone	OH	Me	OMe	H	OMe	H	OMe	H	C. renigera	[49]

36	1,3-Dihydroxy-5,7-8-trimethoxy-2-methyl anthraquinone	OH	Me	OH	H	OMe	H	OMe	OMe	C. sophera
37	1,3,5,8-Tetrahydroxy-6,7-dimethoxy-2-methyl anthraquinone	OH	Me	OH	H	OH	OMe	OMe	OH	C. renigera
38	Sopheranin	OH	Me	OH	H	H	OH	$CH=CH_2$	OH	C. ophera
39	Fallacinol	OH	H	CH_2OH	H	H	OMe	H	OMe	S. didymobotry
40	Parietinic acid	OH	H	COOH	H	H	OMe	H	OH	S. didymobotry
41	Parietinic acid ester	OH	H	COOMe	H	H	OMe	H	OH	S. didymobotry
42	Nataloe-emodin	OH	H	Me	H	H	H	OH	OH	S. longeracemos
43	Rhein methyl ester	OH	H	COOMe	H	H	H	H	OH	S. didymobotrya
44	1,3,6,7,8-Pentahydroxy-4-methoxy-2-methyl-anthraquinone	OH	Me	OH	OMe	H	OH	OH	OH	C. javanica

dix 2 Anthrones of the Leguminosae

Name	Structure								Source	Ref.
										
	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8		
Chrysophanol-9-anthrone	OH	H	Me	H	H	H	H	OH	C. siamea	[15]
Physcion-9-anthrone	OH	H	Me	H	H	OMe	H	OH	C. torosa	[46]

Appendix 3 Pre-anthraquinoes of the Leguminosae

No	Name	Structure			Source	Ref.
						
		R^1	R^2	R^3		
47	Torosachrysone	H	H	H	*C. torosa*,	[48]
					C. didymobotrya,	[12]
					C. singueana	[53]
48	Germitorosone	H	Me	H	*C. torosa*	[54]
49	Methylgermitorosone	OH	Me	Me	*C. torosa*	[55]
50	Germichrysone				*C. torosa*	[55]

Appendix 4 Anthranoid dimers of the Leguminosae

No	Name	Source	Ref.
51	Cassiamin C (2,2′-bichrysophanol)	*C. siamea*	
		C. occidentalis	[56]
52	Cassiamin A (2,2′-Chrysophanol-emodin)	*C. siamea*	
		C. occidentalis	[56]
53	Aloe-emodin-10,10′-bianthrone	*C. senna*	[15]
54	Palamidin D (chrysophanol-physcion-10,10′-bianthrone)	*C. occidentalis*	[13]
		S. longiracemosa	
55	Cassiamin B (2,2′-biemodin)	*C. siamea*	[56]
56	Chrysophanol-10,10′-bianthrone	*C. garrettiana*	[46]
57	Siamianin (4,4′-bichrysophanol)	*C. occidentalis*	[46]
58	Chrysophanol-9,9′-bianthrone	*C. garrettiana*	[46]
59	Rhein-9,9′-bianthrone	*Cassia* spp.	[15]
60	Phlegmacines A_2 and B_2 (7,10′-bitorosachrysone)	*C. torosa*	[27]
61	Anhydrophlegmacin-9,10-quinones A_2 and B_2 (7,10′-physcion-torosachrysone)	*C. torosa*	[27]

Appendix 4 (*contd.*)

No	Name	Source	Ref.
62	Anhydrophlegmacin B_2 (7,10′-physcionanthrone-torosachrysone)	*C. torosa*	[38]
63	Torosanin (7,5′-physcionanthrone-torosachrysone	*C torosa*	[38]
64	Floribundone-1 (7,5′-biphyscion)	*S. septemtrionalis*	[13]
		S. multiglandulosa	[14]
65	Floribundone-2 (7,5′-physcionanthrone-physcion)	*S. septemtrionalis*	[13]
66	Chrysophanol-isophyscion-10,10′-bianthrone	*S. longiracemosa*	[13]
67	Physcion-10,10′-bianthrone	*C. torosa*	[38]
		S. longiracemosa	[13]
68	10-Hydroxy-5,7′-(chrysophanolanthrone)-chrysophanol	*S. longiracemosa*	[13]
69	Siamiadin (4,4′-chrysophanol-emodin)	*C. siamea*	[46]

Appendix 5 Anthranoid glycosides of the Leguminosae

No	Name	Source	Ref.
70	Aloe-emodin-8-mono-β-D-glucose	*Cassia* spp.	[15]
71	Rhein-8-mono-β-D-glucose	*C. occustifolia*	[15]
72	Sennosides A and B (Birhein-9-anthrone-8,8′-diglucoside)	*Cassia* spp.	[15]
73	Sennosoides C and D (Aloe-emodin-rhein-bianthrone-8,8′-diglucoside)	*C. angustifolia*	[15]
74	Chrysophanol-1-O-β-gentiobiside	*C. tora*	[46]
75	Cassialin(10-hydroxy-10-C-D-glucosylchrysophanol-,anthrone)	*C. gerrettiana*	[57]
76	Physcion-1-O-β-D-glucoside	*Cassia* spp.	[46]
77	Physcion-1-glucosylrhamnoside	*Desmodium pulchellum*	[46]
78	Physcion-8-gentiobioside	*C. torosa*	[46]
79	Physcion-8-galactoside	*C. laevigata*	[46]
80	Physcion-8-digalactoside	*C. laevigata*	[46]

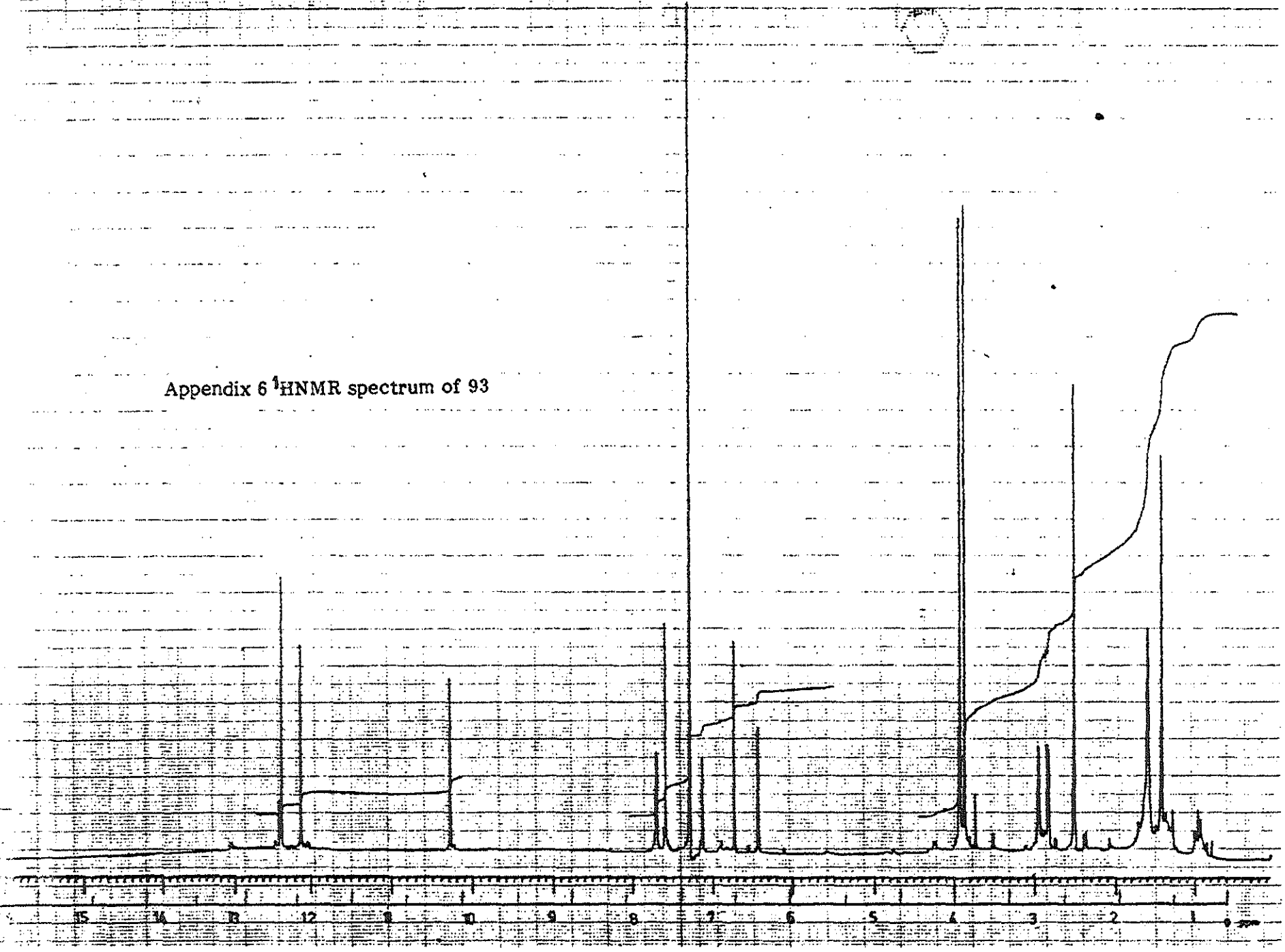
Appendix 5 (*contd.*)

No	Name	Source	Ref.
81	5-Hydroxideemodin-8-O-rhamnoside	*C. javanica*	[46]
82	1,3,5-Trihydroxy-8-methoxy-2-methyl-anthraquinone-3-O-β-D-glucoside	*C. alata*	[46]
83	1,3,8-Trihydroxy-6-methoxy-2-methyl-anthraquinone-3-O-rutinoside	*C. multijuga*	[46]
84	1,3-Dihydroxy-6-,8-dimethoxy-2-methyl-anthraquinone-1-O-glucoside	*C. multijuga*	[46]
85	1,3,5,8-Tetrahydroxy-6,7-dimethoxy-2-methylanthraquinone-rhamnoside	*C. renigera*	[46]
86	1,3-dihydroxy-6,8-dimethoxy-2-methyl-anthraquinone-1-O-rutinoside	*C. multijuga*	[46]
87	1,5,8-Trihydroxy-6,7-dimethoxy-2-methyl-anthraquinone-3-O-α-L-(-)rhamnopyranoside	*C. renigera*	[49]
88	1-Hydroxy-8-methoxy-2-methylanthraquinone-3-O-α-L-(-)rhamnopyranoside	*C. renigera*	[49]

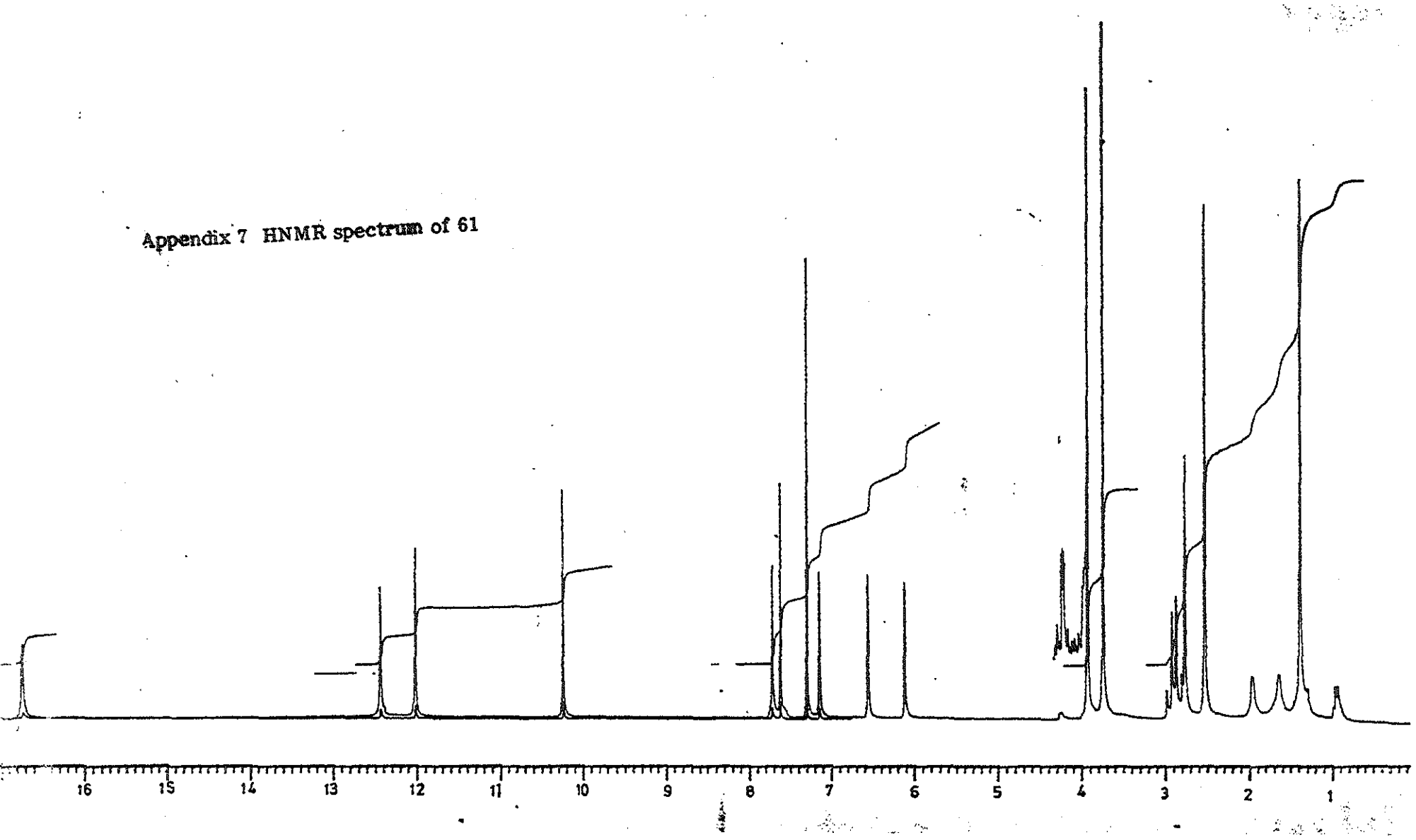
Appendix 5 (*contd.*)

No	Name	Source	Ref.
89	1,5-Dihydroxy-4,7-dimethoxy-2-methyl-anthraquinone-3-O-L(-)rhamnoside	*C. javanica*	[52]
90	Physcion-8-O-α-L-xylopyranoside	*C. marginata*	[49]
91	Emodin-8-O-α-L-arabinopyranoside	*C. marginata*	[49]
92	1,3-Dihydroxy-2-methylanthraquinone-8-O-α-arabinopyranoside	*C. marginata*	[49]

Appendix 6 ^{1}HNMR spectrum of 93



Appendix 7 HNMR spectrum of 61



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