Table 1. Sterols and triterpenes from holly flowers and leaves

Peak	r*	M^+(m/e)	Structural assignment	% of total fraction‡ Kilbarchan flowers ♂30	Kilbarchan flowers ♂3	Kilbarchan flowers ♀3	Kilbarchan leaves ♂3	Kilbarchan leaves ♀3	Garscube leaves ♂	Garscube leaves ♀
1		458	cholesterol	tr			tr	4.2	—	2.2
2	4.2	472	24-methylcholesterol	1.5	1.3	3.9	1.1	—	tr	—
3	4.5	484	24-ethyl-5,22-cholestadien-3β-ol	3.2	5.5	11.3	3.9	2.8	1.2	1.4
4	5.05	(a) 486 (b) 484	24-ethylcholesterol 5,25-diene?	62.6	79.1	84.8	56.3	61.8	29.9	27.4
5	5.86	(a) 486 (b) 484	24-ethylcholesterol† 24-ethylidenecholcsterol¶	8.9	tr	—	4.7	9.0	1.7	4.5
6	6.0	498	pentacyclic triterpene§ (amyrin type)	16.2	6.3	tr	29.7	18.8	8.6	23.4
7	6.6	498	pentacyclic triterpene§ (amyrin type)	1.35	2.4	—	tr	tr	7.7	7.6
8	7.3	496	pentacyclic triterpene§ (amyrin type)	6.25	5.4	—	5.3	3.4	50.8	33.5

* $C_{28}H_{58}$ = 1.0. † Carried over into mass spectrometer from previous peak. ‡ By triangulation, tr = trace, —not detected. ¶ In leaves this peak appears to largely consist of triterpenoid material. § Usually a broad peak (2 or more isomeric compounds).

EXPERIMENTAL

Holly was collected from 3 sources, a male tree, Tandlehill Road, Kilbarchan (30th May 1976: ♂30) National Grid Reference NS 409623, and trees in the garden of Riversdale, Tandlehill Road, Kilbarchan, National Grid Reference NS 409623 (3rd June 1976: ♂, ♀3) and the Garscube Estate, Glasgow (8th June 1976), National Grid Reference NS 551704. Leaf material was air-dried (90°) and crushed, whereas flowers were stored in MeOH. Extraction ($CHCl_3$–MeOH), sterol isolation (TLC on Si gel $CHCl_3$) and GLC (of TMS ethers on OV-17) were by standard methods. GC–MS was performed on a V.G. Micromass 16F GC–MS (jet separator) with an OV-17 column. Peaks 6 and 7 both exhibited molecular ions at *m/e* 498 with base peak *m/e* 218 and prominent ions at *m/e* 203, 190, 189. Peak 8 had M^+ 496, and base peak *m/e* 216.

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STEROLS OF LILIACEAE

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Key Word Index—*Cordyline indivisa; Allium cepa; A. fistulosum* var. *caespitosum*; Liliaceae; sterols.

Cordyline indivisa Kunth, an ornamental plant, was collected on the campus of Tokyo Gakugei University in November 1974. There has been no previous work on the sterols of this plant.

Preparative Si gel TLC [1] of the unsaponifiable matter (2.20 g) of the lipid (89 g), Soxhlet extracted by CH_2Cl_2 from dried and ground seeds (616 g), gave 4,4-dimethyl- (110 mg), 4-monomethyl- (210 mg) and 4-desmethyl- (530 mg) sterol fractions. The following sterols were tentatively identified by GLC (OV-17) [2] and GC–MS: cycloartanol (approximately 44%), cycloartenol (33%), and 24-methylenecycloartanol (3%) in the 4,4-dimethylsterol fraction [3,4]; 31-norlanostenol and 4α-methylzymostenol (unresolved by GLC, 13%) [5,6], lophenol (56%) [5,6], 31-norcycloartenol (14%) [5,7], gramisterol (24-methylenelophenol) [8] and cycloeucalenol [9] (unresolved, 2%), and citrostadienol (1%) [8] in the 4-monomethylsterol fraction; and cholesterol (13%), cholest-7-enol (12%), campesterol (9%), stigmasterol (17%), sitosterol (49%), and 28-isofucosterol (trace) in the 4-desmethylsterol fraction [10]. The 4-desmethylsterol fraction was further resolved as its acetate by preparative $AgNO_3$–Si gel TLC. Traces of cholestanol (M^+, *m/e* 430), campestanol (M^+, *m/e* 444), stigmastanol (M^+, *m/e* 458) and an unidentified sterol (M^+, *m/e* 442) also were found as their acetates in the fraction from the least polar faint zone.

Allium cepa L. (onion) has previously been reported to contain cholesterol, brassicasterol, campesterol, stigmasterol and sitosterol in the bulbs [11]. In the present work preparative Si gel TLC of the unsaponifiable matter (1.35 g) of the lipid (5.2 g), extracted from the milled and dried bulbs (337 g) by CH_2Cl_2, afforded 4,4-dimethyl- (210 mg), 4-monomethyl- (230 mg) and 4-desmethyl-

(450 mg) sterol fractions. The following constituents were tentatively identified by GLC and GC–MS as described above: cycloartanol (approximately 11%), cycloartenol (75%) and 24-methylenecycloartanol (4%) in the 4,4-dimethylsterol fraction; 31-norlanostenol and 4α-methylzymostenol (unresolved, 25%), lophenol (43%), 31-norcycloartenol (12%), and gramisterol and cycloeucalenol (unresolved, 3%) in the 4-monomethylsterol fraction; and cholesterol (14%), cholest-7-enol (1%), campesterol (8%), stigmasterol (trace), sitosterol (68%), and 28-isofucosterol (9%) in the 4-desmethylsterol fraction.

Allium fistulosum var. *caespitosum* Makino (shallot) was reported to contain cholesterol, campesterol, stigmasterol, and sitosterol in the plant separated from the root [12].

Preparative Si gel TLC as described above of the unsaponifiable material (2.44 g) of the lipid (13 g), extracted from the milled and dried plant (1250 g), separated from the root, by CH_2Cl_2, gave 4,4-dimethyl- (240 mg), 4-monomethyl- (290 mg) and 4-desmethyl- (370 mg) sterol fractions. Tentative identification of the sterols in each fraction was made by GLC and GC–MS: cycloartanol (approximately 33%), cycloartenol (39%) and 24-methylenecycloartanol (24%) in the 4,4-dimethylsterol fraction; 31-norlanostenol and 4α-methylzymostenol (unresolved, 24%), lophenol (30%), 31-norcycloartenol (15%), gramisterol and cycloeucalenol (unresolved, 4%), and citrostadienol (trace) in the 4-monomethylsterol fraction; and cholesterol (32%), cholest-7-enol (2%), campesterol (4%), stigmasterol (1%), sitosterol (48%), and 28-isofucosterol (13%) in the 4-desmethylsterol fraction.

A marked similarity in the composition of the sterol mixture is observed among these three Liliaceae plants. The C-24 unalkylated sterols, especially those with a saturated side chain, were abundant in the 4,4-dimethyl- and 4-monomethyl-sterol fractions, and a remarkable amount of cholesterol was found in the 4-desmethylsterol fraction. This composition pattern of sterols is markedly different from those observed for the seed sterols of a number of other higher plants previously studied in this laboratory [1, 5, 13, 14]: the 4-monomethylsterol fraction consists almost exclusively of C-24 alkylated sterols and the 4-desmethylsterol fraction contains at most a very small amount of cholesterol. One exception is red pepper, *Capsicum annuum* (Solanaceae), [5], which shows a sterol composition similar to that of the three Liliaceae plants. It is now well known that liliaceous and solanaceous plants contain a notable amount of C_{27} steroidal sapogenins and alkaloids and that cholesterol is the main biosynthetic precursor of these sapogenins and alkaloids [15–17]. These facts being taken into account, it seems to be of special interest that cholesterol occurs in an unusually large proportion in the 4-desmethylsterol fractions of the three Liliaceae plants and a Solanaceae plant, *C. annuum* [5].

A considerable amount of cholest-7-enol as well as cholesterol was found in the 4-desmethylsterol fraction of *C. indivisa* seeds. This appears to be the first record of such a high content of this sterol in higher plants.

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BACOGENIN-A_3: A NEW SAPOGENIN FROM *BACOPA MONNIERA*

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Key Word Index—*Bacopa monniera*; Scrophulanaceae; bacogenin A_3; triterpenoids.

Abstract—The structure of bacogenin A_3, one of the sapogenins of the bacosides has been established by various chemical and spectral methods.

INTRODUCTION

The acid hydrolysis of the crystalline saponins of *Bacopa monniera* gave rise to a mixture of four bacogenins [1]. Bacogenin A_4 was identified as ebelin lactone [2]