This identification was confirmed by total acid hydrolysis, partial acid hydrolysis and treatment with β-glucosidase to give D-glucose and aureusidin (4,6,3′,4′-tetrahydroxyaurone). D-glucose was identified as above; aureusidin was identified by paper co-chromatography with authentic sample (solvents A, H and P) and UV-spectral analysis with shift reagents[8].

Results and discussion. Although several natural products based upon 3,4,2′,4′,6′-pentahydroxychalcone are known[11], pigment **1** is the first chalcone whose substitution pattern is related to that of the flavanone homoeriodictyol. Cernuoside (**2**) is reported for the first time in the Leguminosae; this anthochlor pigment was first isolated from *Oxalis cernua*[12] (Oxalidaceae) and later found in 4 species of Gesneriaceae (*Chirita micromusa*[13], *Cyrtandra oblongifolia*[14], *Didymocarpus malayanus*[14] and *Petrocosmea kerrii*[15]) and in the Plumbaginaceae (*Limonium bonduelli*[13] and *Limonium* cv. Gold Coast[16]). It is interesting to note that anthochlor pigments **1** and **2** as well as anthochlors (isosalipurposide and chalcononaringenin 2′-xyloside) previously isolated[7] from *Acacia dealbata* have phloroglucinol A-ring structures. The occurrence of 4 such pigments in this plant is quite exceptional since resorcinol based-A-ring anthochlors are considered a biochemical characteristic of the family Leguminosae[11].

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Starfish saponins VII. Structure of luzonicoside, a further steroidal cyclic glycoside from the pacific starfish *Echinaster luzonicus*[1,2]

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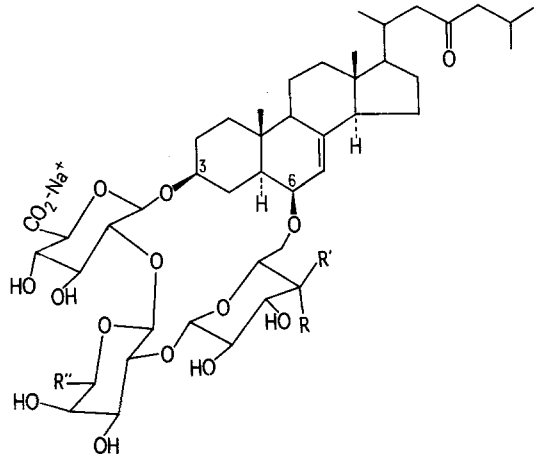
Summary. On the basis of comparative chemical and spectral data, the structure of the major saponin, luzonicoside, from the starfish *Echinaster luzonicus* has been elucidated as **2.** This is a further example of a novel class of steroidal cyclic glycoside from starfish of the genus *Echinaster.* Its structure includes a Δ^7, 3β,6β-dioxygenated-23-oxosteroidal moiety, already found in the saponins of *Echinaster sepositus,* and a trisaccharide moiety, β-D-galactopyranosyl-(1 → 2) α-L-arabinopyranosyl-(1 → 2)-β-D-glucuronopyranosyl, bridging C-3 and C-6 of the steroid.

Recently we have elucidated[6] the structure of the major saponin, sepositoside A, from *Echinaster sepositus* as **1.** On very mild acid treatment (1 *N*-HCl, r.t.) it gives the corresponding opened glycoside **3**, while it is hydrolyzed to its sugars and the 3β-hydroxy-5α-cholesta-8,14-dien-23-one[7], by prolonged acid treatment. The structures of the minor saponins from the same sources possess the same cyclic trisaccharide moiety bridging C-3 and C-6 of the steroid, and the differences reside in the steroidal side-chains, characterized by epoxide functionalities at C-22 and C-23 (part structures **5**–**7**)[8].

In this paper we describe the discovery of a further example of this novel class of steroidal cyclic glycoside from a starfish of the same genus, *E. luzonicus,* collected near Nouméa, Nouvelle Calédonie. The extraction and isolation of the saponins has followed the same procedure used before[6]. Fresh animals (4 kg), collected in october 1979, were extracted with water and the extracts were lyophilized (290 g). After removal of fat materials by washing with $CHCl_3$, the saponins were recovered from the aqueous solution by Amberlite XAD-2 and purified by silica gel column chromatography followed by reverse phase HPLC[9] (C-18 μ-Bondapak; CH_3OH:H_2O, 55:45) to give 0.75 g of luzonicoside.

Luzonicoside (**2**) analyzed for $C_{44}H_{67}O_{17}Na$, was levorotatory, $[\alpha]_D - 66°$ (H_2O), and was indistinguishable from sepositoside A (**1**) in TLC and HPLC. On acid hydrolysis it yielded the 3β-hydroxy-5α-cholesta-8,14-dien-23-one, but, unlike **1**, D-galactose, L-arabinose and D-glucuronic acid. In the 270-MHz NMR-spectrum (DMSO) it showed a broad signal at δ5.47 ($W^{1}/_{2} = 12$ Hz) corresponding to the olefinic proton at C-7, 2 methyl singlets at δ0.556 and 0.825 corresponding to CH_3-18 and CH_3-19, respectively and methyl doublets at δ0.85 and 0.83 for CH_3-21, -26 and -27. The same signals were also observed in the spectrum of **1**; the spectrum of **2** also contained 3 doublets assigned to the anomeric protons at δ4.32 (J = 7.5 Hz), 4.65 (J = 7.5 Hz) and 5.05 (J = 7.0 Hz). Similarly the comparison of the ^{13}C-NMR spectrum of **2** with that of the known **1** indicated that the steroidal parts of the molecules were identical (all resonances associated with the steroidal carbons had identical

δ's and have already been described for **1**[6]); differences were observed in the sugar carbon region and in the spectrum of **2** the sugar carbon atoms resonated at 103.4, 98.0 and 96.3 ppm (anomerics), 176.5 (CO_2^-), 64.1 (C(5) arab) and between 70.7 and 78.8 ppm (remaining carbons and C-3 and C-6 of the aglycone). In analogy with **1**, on mild acid treatment (1 N-HCl, r.t.) luzonicoside yielded the corresponding opened glycoside, **4**, $[\alpha]_D$ −37° (MeOH). Direct comparison of its spectral properties UV, λ_{max} 259, 251 (ε, 20,500), 244; ^{1}H-NMR, δ 5.27 (bd, J = 10 Hz, H-6), 6.12 (dd, J = 10, 3 Hz, H-7), 0.66 and 0.96 (each s, CH_3-19 and -18); ^{13}C-NMR (all resonances associated with the steroidal carbons are virtually superimposable in the spectra of **3** and **4**) with those of the opened glycoside **3**[6] established the 5α-cholesta-6,8(14)-dien-23-one structure for the aglycone. Permethylation of **4** with CH_3I-DMF-NaH[6] gave a nona-O-methyl derivative, M^+/e 994, which revealed mass fragment ions (m/e 219 → 187 → 155 → 111 due to the terminal permethylated hexose and m/e 379 → 347 → 315 due to the permethylated galactose-arabinose residue) indicative for the sugar residues sequence, gal → arab → glucur-1-O-aglycone, and gave, on acid hydrolysis, 2,3,4,6-tetra-O-methylgalactose (TLC and GLC), a di-O-methylarabinose and a di-O-methylglucuronic acid. $NaBH_4$ reduction and acetylation with Ac_2O and pyridine[10] of the di-O-methylarabinose (separated from the methylated sugars mixture by SiO_2-PLC in CH_2Cl_2-aceton, 2:1) afforded 1,4,5-tri-O-acetyl-2,3-di-O-methylpentitol (identified by mass spectrometry, m/e 233, 189, 161, 129, 117, 101, 99, 87[10]) indicative for 1 → 2 or 1 → 4 linkage galactose-arabinose. The choice in favour of the 1 → 2 linkage has been made on the basis of the appearance in the ^{13}C-NMR spectrum of the glycoside **4** (table) of a high field signal at 68.6 ppm which may only be assigned to HO-C(4) of arabinopyranosyl residue. That arabinose is present in its pyranose form is confirmed by the appearance in the ^{13}C-NMR spectrum of the signal at 65.8 ppm for C(5). The ^{13}C-NMR data also suggested the 1 → 2 linkage arabinose-glucuronate [C(2) carbon shifted downfield by about 10 ppm to 84.0 ppm, whereas the other signals of the glucuronate moiety remained almost unaffected]. With regard to the configuration of the glycoside linkages, on the basis of the downfield shifts of the anomeric carbons (101.7 → 106.4 ppm) and the coupling constants of the anomeric proton signals of **2** (J = 7.0 to 7.5 Hz), the glycosidic linkage of L-arabinopyranose is α, while those of D-galactose and D-glucuronate are β. Thus the structure of the opened glycoside **4** is established to be 3β-hydroxy-5α-cholesta-6,8(14)-dien-23-one-O-β-D-galactopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 2)-β-D-glucuronopyranoside.



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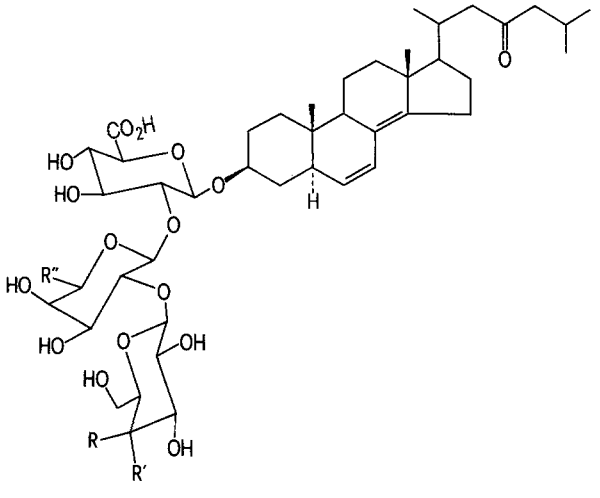
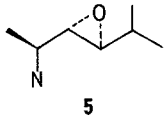
2 R = OH, R' = H, R'' = H



3 R = H, R' = OH, R'' = CH_2OH
4 R = OH, R' = H, R'' = H



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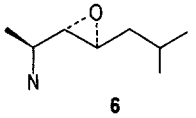

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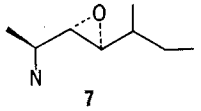

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^{13}C-NMR shifts of sugar carbons in **4*** (CD_3OD, TMS = O)

Sugar carbons	4			Me-glycopyranoside		
	Gal	Arab	Glucur	β-D-gal[11]	α-L-arab[12]	β-D-glucur[6]
1	106.4	103.9	101.7	104.9	104.0	105.9
2	72.5	81.7	84.0	71.8	70.9	74.7
3	73.5	74.9	77.4	73.9	72.5	77.4
4	70.5	68.6	73.2	69.8	68.3	72.8
5	76.4	65.8	77.2	76.2	66.1	76.9
6	62.6	=	172.7	62.1	=	162.1(CO_2CH_3)

* Resonances of the aglycone carbons have identical δ's to these described for **3**[6].

The lack of the signal for a primary hydroxyl carbon atom in the ^{13}C-NMR spectrum of the intact glycoside indicated a substitution at the HO-C(6) carbon of galactose and led to the cyclic structure **2** for the *E. luzonicus* major saponin, luzonicoside. We would note that in both sepositoside A(**1**) from *E. sepositus,* and luzonicoside (**2**), from *E. luzonicus,* the macrocyclic ring made up by the sugar moiety has the same size and conformation.

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2 Acknowledgments. We wish to thank Mrs M. Pusset, Laboratoire des Plantes Médicinales du C.N.R.S., Nouméa, for the extraction of starfish and the divers of the Centre O.R.S.T.O.M. de Nouméa for collection.
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9 HPLC-chromatograms of *E. sepositus* and *E. luzonicus* saponins are almost indistinguishable. Both chromatograms contained 3 peaks of which the central one corresponded to the major component. In the *E. luzonicus* it accounts for more than 90% of the total saponin content. The 2 minor saponins were obtained still in admixture with the major one and, in analogy with the minor saponins of *E. sepositus,* on acid hydrolysis, they gave 24-nor-22(R)-chloro-5α-cholesta-8,14-diene-3β,23(S)-diol (more polar saponin) and 22(R)-chloro-5α-cholesta-8,14-dien-3β,23(S)-diol along with minor amounts of 27-nor-24-methyl-22(R)-chloro-5α-cholesta-8,14-dien-3β,23(S)-diol (less polar saponin)[13]. The ^{13}C-NMR spectra of both mixtures confirmed the origin of these chlorohydrins from their corresponding epoxides (part-structures **5**–**7**).
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Absolute configuration of (+)-1,4-diphenyl-2,3-butanediol[1]

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Summary. The absolute configuration of the title compound, isolated earlier from bull testicular tissue, has been determined to be (2S,3S) by synthesis of the natural diol from L-(+)-tartaric acid.

In 1963 Neher reported the isolation of (+)-1,4-diphenyl-2,3-butanediol (**1**) from the testicular tissue of bulls and rats[2]. The occurrence of such a novel structure, apparently biogenetically unrelated to the usual steroidal androgens, was surprising and elicited interest in its possible physiological role. Neher reported that the diol was not found in the adrenals, liver, or ovaries, though it was later detected in the postmortem human liver[3]. The diol is secreted at a low rate in the spermatic venous blood of the gonadotrophic stimulated dog[4].

The diol is practically free of estrogenic and androgenic activity, although at high concentration it weakly inhibited testicular secretion of testosterone[2,4]. S.c. administration in gonadectomized, adult male rats did not depress serum LH or FSH levels,[5,6] but local implanation of the diol in the median eminence of the hypothalamus resulted in a significant elevation of serum FSH[6]. On the basis of these findings Iturriza et al.[6] postulated a physiological role for the diol in the control of FSH release.

Because of the possible importance of this substance in reproductive endocrinology and the dependence of biological activity on stereochemical configuration, we have determined the absolute configuration. The similarity of the chiral centers to those in tartaric acid prompted us to synthesize the diol from L-(+)-tartaric acid, using the reactions shown in the scheme.

L-Tartaric acid was converted to the diethyl ester acetonide **2**. Following published procedures, **2** was reduced with lithium aluminum hydride to 2,3-O-isopropylidene-L-threitol (**3**) and then converted to ditosylate **4**. Displacement of the tosylate functions by phenyl was achieved with lithium diphenyl cuprate[7], and the resulting acetonide **5** was hydrolyzed by dilute acid to afford diol **1**. The synthetic product had the same melting point, IR-spectrum, and optical rotation as reported for the naturally occurring diol. Since the absolute configuration of (+)-tartaric acid has been defined by anomalous X-ray dispersion measurements[8] and the reactions used in the correlation sequence do not affect the asymmetric centers, the natural (+)-diol has the (2S,3S) configuration.

Experimental section. 1,4-Diphenyl-2,3-O-isopropylidene-L-threitol (**5**). To a solution of 3.0 g of cuprous iodide in 10 ml of dry ether, stirred at 0 °C under argon was added dropwise 20 ml of a 20% solution (2.1 M) of phenyl lithium in 75% benzene /25% hexane (Foote Chemical Co). A solution of 1.93 g of 2,3-O-isopropylidene-L-threitol ditosylate (**4**)[9], mp 90–92 °C, in 12 ml of ether and 3 ml of THF was added dropwise to the resulting green solution and the mixture was stirred at 25 °C for 2 h. Saturated aqueous ammonium chloride was added and the volatile solvents were removed at reduced pressure. The aqueous residue was extracted with several portions of ether, and the