Phytochemistry, 1973, Vol. 12, pp. 2571 to 2578. Pergamon Press. Printed in England.

REVIEW ARTICLE

β-AMYRIN TRITERPENOIDS

ROBIN B. BOAR and JOHN ALLEN*

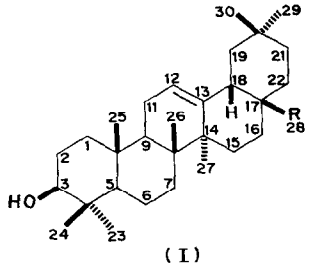
Department of Chemistry, Chelsea College, London SW3 6LX

(*Received* 16 *June* 1973. *Accepted* 2 *July* 1973)

Key Word Index—β-Amyrin triterpenoids; oxygenation patterns; artefacts; review.

Abstract—The natural occurrence of β-amyrin triterpenoids is reviewed. The distribution of functiona groups within these compounds is tabulated and commented upon. The generation of artefacts is surveyed.

TRITERPENOIDS of the β-amyrin group are widely distributed throughout the plant kingdom.[1-3] Table 1 contains all compounds† of known structure with the basic skeleton 3β-hydroxyolean-12-ene (I; R=Me) or 3β-hydroxy-13β,28-epoxyoleanane (II). A small number of corresponding 3α-hydroxy,[4] 3-keto,[5] or ring A-*seco*[6] compounds are also known.



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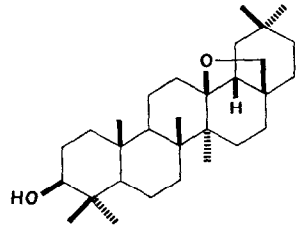

(II)

* Present address: Department of Biochemistry, Union International Research Centre, St. Albans, Hertfordshire.

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Many of the compounds of Table 1 are sapogenins. These have usually been isolated by hydrolysis of a saponin under fairly drastic acid conditions. The use of alternative hydrolysis procedures (milder acid;[7] sodium periodate;[8] various enzyme systems[9]) is to be preferred, and has shown that a number of supposed sapogenins are artefacts. These cases are summarized in Table 2. Particular attention has been paid to the widespread 12-en-28-ol system (e.g. I; R=CH_2OH) and the 13β,28-ether system (e.g. II) from which the former is derivable by acid treatment. Present evidence suggests that both of these systems can represent genuine sapogenins. Thus, either acid or sodium periodate hydrolysis of the saponin from *Primula japonica* yields dihydropriverogenin A (I; R=CH_2OH, 16α,22α-diol). In the former case this is accompanied by primulagenin A (I; R=CH_2OH, 16α-ol), but in the latter by protoprimulagenin A (II; 16α-ol).[7]

Table 3 shows the distribution of oxygen functions within the 110 compounds of Table 1. These statistics should be relevant to future structure determinations and to the development of biosynthetic theories. Attention is drawn to the following points: (1) oxygenation is particularly common along the two edges of the molecule comprising C-16,28,22,21,30 and C-2,3,23,24, whilst at other sites it is observed rarely if at all. More detailed patterns are often apparent for the compounds from plants which are botanically closely related.[10] At some positions (e.g. C-2, C-16, C-22) the pattern is markedly different for acids and non-acids; (2) all 13β,28-ethers are also oxygenated at C-16; (3) the high incidence of C-28 oxygenated compounds suggests that the conversion of β-amyrin into erythrodiol will prove to be a primary step in many biosynthetic pathways;[11] (4) the occurrence of additional double bonds within the β-amyrin skeleton is rare. Saikogenins E, F and G are formally derivable from a 12-ene-11,28-diol system.[12] Bassic acid (from *Madhuca longifolia*, at least) and aegiceradiol are artefacts (see Table 2). We suggest that soyasapogenol C (21-ene) is probably an artefact of soyasapogenol B (21-ol), and that soyasapogenol E (21-ketone) might be similarly derived from soyasapogenol A (21,22-diol).

TABLE 1. NATURALLY OCCURRING β-AMYRIN TRITERPENOIDS

Trivial name	Hydroxyl substituents	M.p. (°)*	$[\alpha]_D$ (°)†	Occurrence	Ref.
	(I) *Alcohols* (I; R = Me)				
β-Amyrin	—	199–200	88	Widespread	13
11α-Hydroxy-β-amyrin	11α	200–210	—	*Salvia glutinosa*	14
Manilադiol	16β	220–221	68	Manila elemi resin *Escontria chiotilla* *Myrtillocactus eichlamii*	15
Sophoradiol	22β?	219–220	113	*Sophora japonica*	16

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TABLE 1—*continued*

Trivial name	Hydroxyl substituents	M.p. (°)*	$[\alpha]_D$ (°)†	Occurrence	Ref.
Soyasapogenol C	24 (21-ene artefact?)	240	65	Various	17
Erythrodiol	28	235–237	76	Various	15
Primulagenin A	16α,28	236–237	56	Various	18
Longispinogenin	16β,28	247–249	53	Various Cactaceae *Bupleurum falcatum*	10a,19
Soyasapogenol B	21α,24	260–261	90	Various	17
22α-Hydroxyerythrodiol	22α,28	279–282 ($\frac{1}{2}H_2O$)	37 P	*Camellia sasanqua*	18
Barringtogenol	2α,23,28	290–291	18 P	*Barringtonia racemosa* *Terminalia tomentosa*	20
Castanogenol	28,23,28	263–265	90	*Castanospermum australe*	21
Dihydropriverogenin A =	16α,22α,28	265–267	23 M	Various—see Ref. 24	22
Camelliagenin A =		290–293	20 E		23
Theasapogenol D =		273–275	30 E		24
A_2-Barrigenol					
Chichipegenin	16β,22α,28	321–323	43	Various Cactaceae	25
Soyasapogenol A	21α,22α,24?	310–313	103	*Soja hispida*	17
16-Desoxybarringtogenol C	21β,22α,28	288–291	50 E	*Aesculus turbinata*	26
A_1-Barrigenol	15α,16α,22α,28	300–302	4	Various—see Ref. 27	27
Barringtogenol C =	16α,21β,22α,28	315–320	34 D	Various—see Ref. 27	28
Aescinidin =		302–308	33 D		
Jegosapogenol A =		326–330	30 P		
Theasapogenol B =		278–284	11 P		
R_2-Barrigenol					
Camelliagenin C =	16α,22α,23,28	262–263	37 E	*Camellia japonica*	23,29
Theasapogenol C		264–266	—	*Camellia sasanqua* *Thea sinensis*	24
Gymnestrogenin	16β,21β,23,28	288–289	54 M	*Gymnema sylvestre*	30
Tanginol	6β,7β,16β,23,28	283–284	9 E	*Barringtonia acutangula*	31
R_1-Barrigenol	15α,16α,21β,22α,28	310–312	41 D	Various—see Ref. 27	27
Theasapogenol A	16α,21β,22α,23,28	301–303	14 P	*Camellia sasanqua* *Thea sinensis*	32
Protoaescigenin	16α,21β,22α,24,28	303–311	32 D	*Aesculus turbinata* *A. hippocastanum*	33
Gymnemagenin	16β,21β,22α,23,28	328–335	53 M	*Gymnema sylvestre*	34
	Substituents: Hydroxyl / Carbonyl				
	(2) *Aldehydes and Ketones* (I; R = Me)				
Camelliagenin B	16α,22α,28 / 23	200–205	48 E	*Camellia japonica* *C. sasanqua* *Thea sinensis*	23
Theasapogenol E =	16α,21β,22α,28 / 23	260–263	34 P	Various *Camellia* species	24
Camelliagenin E		270–273	64		35
Camelliagenin D (artefact?)	16α,21β,22α,28 / 24	250–258	39	Various *Camellia* species	35

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TABLE 1—*continued*

Trivial name	Hydroxyl substituents			M.p (°)	$[\alpha]_D$ (°)†	Occurrence	Ref.
Oleanolic aldehyde	—		28	168–172	72	*Heliabravoa chende* *Mangifera indica*	36
Primulagenin D	16α		28	217–218	25	Various *Primula* species	22
Gummosogenin	16β		28	251–252	28	*Machaerocereus gummosus*	37
Priverogenin A	16α,22α		28	198–202	−4	Various *Primula* species	22
Glycyrrhetol	30		11	252–254	87	*Glycyrrhiza glabra*	38
Soyasapogenol E	24		21	234–236 (diacetate)	31	*Soja hispida*	39
Armillarigenin	16α,28		21	299–301	11 E −11 P	*Jacquinia armillaris*	40
	Substituents						
	Hydroxyl	Carbonyl	Double Bond				
				(3) *Ethers* (II)			
Protoprimulagenin A	16α	—	—	272–273	13	*Primula sieboldi*	7
Priverogenin B	16α,22α	—	—	265–269 280–283	−8 M	Various *Primula* species	22,41
Saikogenin E	16β	—	11	283	108	*Bupleurum falcatum*	19
Saikogenin G	16α,23	—	11	238–245	83	*Bupleurum falcatum*	19,42
Saikogenin F	16β,23	—	11	265–273 ($\frac{1}{2}CHCl_3$)	96	*Bupleurum falcatum*	19
Aegicerin	—	16	—	254–256	−24	*Aegiceras majus* *Primula sieboldi*	7,43
Anagalligenone B	23	16	—	300–310	−25 P	*Anagallis arvensis*	44
Cyclamiretin A	16α	30	—	202–204	8	*Cyclamen europaeum*	45
Cyclamigenin B	—	16,30	—	295–296	−10	*Cyclamen europaeum*	46
	Substituents						
	Hydroxyl		Carboxyl				
				(4) *Acids* (I; R = Me)			
Commic acid C	2β		23	343–345	—	*Commiphora pyracanthoides*	47
β-Peltoboykinolic acid	—		27	220–222	114	*Peltoboykinia tellimodes*	48
Oleanolic acid	—		28	303–306	78	Widespread	3
Crategolic acid = Maslinic acid	2α		28	267–269	43 P	Various	49
Sumaresinolic acid	6β		28	298–299	54	Sumatra gum benzoin *Myroxylon balsamum*	50
Rubusic acid	7α		28	265–270	—	*Rubus moluccanus*	51
Echinocystic acid	16α		28	305–312	28 E	Various—see Ref 3	52
Cochalic acid	16β		28	303–306	58 D	Various *Myrtillocactus* species	53
Siaresinolic acid	19α		28	279–280	39 E	Siamese gum benzoin *Randia spinosa*	54,55
Spinosic acid	19β		28	270–272	13	*Randia spinosa*	55
Machaerinic acid = Stryphnodendron sapogenin L	21β artefact?		28	232–234 (methyl ester)	76	Various	56

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TABLE 1—*continued*

Trivial name	Hydroxyl substituents		M.p. (°)*	$[\alpha]_D$ (°)†	Occurrence	Ref.
—	22β-angeloyloxy	28	296–298	70	*Lippia rehmanni*	57
Hederagenin	23	28	327–329	81 P	Widespread	3,58
Mesembryanthemoidigenic acid	29	28	305–309	71	*Rhipsalis mesembryanthemoides*	59
Queretaroic acid	30	28	318–323	—	*Lemaireocereus queretaroensis* *L benekei* *Clerodendron serratum*	60
Arjunic acid	2α,19α	28	334–335	20 E	*Terminalia arjuna*	61
Stryphnodendron sapogenin K	2α,21β artefact?	28	236–239	—	*Stryphnodendron coriaceum*	62
Arjunolic acid	2α,23	28	337–340	63 E	Various	63
Bayogenin	2β,23	28	328–330	98 D	*Castanospermum australe* *Planchonella pohlmaniana*	21
Bassic acid	2β,23 (5-ene) artefact?	28	320 dec.	83 P	Various Sapotaceae	64
Entagenic acid	15α,16α?	28	310–315	35 E	*Entada phaseoloides*	65
Acacic acid	16β,21β	28	278–282	—	Various *Acacia* and *Albizzia* species	66
Acerogenic acid	21β,22α	28	308–310	66 E	*Acer negundo*	67
Treleasegenic acid	21β,30	28	280–290	—	*Lemaireocereus treleasei*	68
—	22β-angeloyloxy,24	28	294–298	73 E	*Lippia rehmanni*	57
Terminolic acid	2α,6β,23	28	347	42 E	*Terminalia ivorensis*	69
Tomentosic acid	2α,19β,23	28	328–330	64 E	*Terminalia tomentosa* *Bixa orellana*	70
Protobassic acid	2β,6β,23	28	310–312	23 P	*Madhuca longifolia*	64
Polygalacic acid	2β,16α,23	28	295–300	47 P	*Polygala paenea* *Platycodon grandiflorum*	71
Platycogenic acid C	2β,16β,21β	28	282–288 (dec.)	78 E	*Platycodon grandiflorum*	72
Caccigenin	15α,16β,23?	28	273–275 (methyl ester)	77 M	*Caccinia glauca*	73
24-Hydroxyacerogenic acid	21β,22α,24	28	341–342 (dec.)	70 E	*Acer negundo*	67
Platycodigenin	2β,16α,23,24	28	241–242	35 P	*Platycodon grandiflorum*	71
Myrtillogenic acid	16β,28	29	288–293	84 M	Various *Myrtillocactus* species	74
Liquiridiolic acid	21α,24	29	285–287 (dec.)	45	*Glycyrrhiza glabra*	75
11-Deoxoglycyrrhetic acid	—	30	330	148	*Glycyrrhiza glabra*	76
24-Hydroxy-11-deoxoglycyrrhetic acid	24	30	263–264 (methyl ester)	134	*Glycyrrhiza glabra*	77
Jacquinic acid	16α,28	30	310–312	49 M	*Jacquinia pungens*	78

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TABLE 1—*continued*

Trivial name	Hydroxyl substituents			M p. (°)*	$[\alpha]_D$(°)†	Occurrence	Ref.
	Substituents: Hydroxyl	Carbonyl	Carboxyl				
	(5) *Aldehydo- and Keto-acids* (I; R = Me)						
Gypsogenin	—	23	28	269–270	91 E	Widespread	3
Quillaic acid	16α	23	28	292–293	56 P	Various	79
Momordic acid	—	1	28	274–276	—	*Momordica cochinchinensis*	80
Machaeric acid	—	21	28	309–312	20	*Machaerocereus gummosus*	56
Liquiritic acid	—	11	29	298–303	85	*Glycyrrhiza glabra*	76
24-Hydroxyliquiritic acid	24	11	29	282–286 (dec.)	79	*Glycyrrhiza glabra*	75
Glycyrrhetic acid	—	11	30	300 dec.	163	Various	3
18α-Hydroxyglycyrrhetic acid	18α	11	30	252–255	60 A	*Glycyrrhiza glabra*	81
24-Hydroxyglycyrrhetic acid	24	11	30	247–248 (methyl ester)	142	*Glycyrrhiza glabra*	77
	Substituents: Hydroxyl		Carboxyl				
	(6) *Diacids* (I; R = CO_2H)						
Gypsogenic acid	—		23	> 330	86 M	*Saponaria officinalis*	82
Barringtogenic acid	2α		23	332–334	72 M	*Barringtonia racemosa*	83
Medicagenic acid = Castanogenin	2β		23	349–350 380–382	111 E 107 E	*Medicago sativa* *Castanospermum australe*	84
—	16α		23	250–255 (dimethyl ester)	42	*Saponaria officinalis*	82
Presenegenin	2β,27		23	223–225 (dimethyl ester)	80	*Polygala senega* *P. tenuifolia*	85
Platycogenic acid A	2β,16α,23		24	243–249	74 E	*Platycodon grandiflorum*	72
Platycogenic acid B	2β,16β,21β		24	274–277 (dec.)	101 E	*Platycodon grandiflorum*	72
Cincholic acid	—		27	265–268	118 P	Cinchona bark	86
Serratagenic acid	—		29	> 310	37 P	*Clerodendron serratum*	87
Spergulagenic acid	—		30	347–350	121 P	*Mollugo spergula*	88
Phytolaccagenin	2β,23		30 (CO_2CH_3)	317–318 (dec.)	—	*Phytolacca americana*	89
	Substituents: Lactone	Hydroxyl	Carbonyl				
	(7) *Lactones* (I, R = Me)						
Proceragenin A	28.15β	16α	—	294–296	−13	*Albizzia procera*	90
Dumortierigenin	28 15β	22α	—	292–295	−19	*Lemaireocereus dumortieri*	91
Stryphnodendron sapogenin B	28 21β	—	—	240–243	−16	*Stryphnodendron coriaceum* *Enterolobium contortisiliquum*	92
Stryphnodendron sapogenin F	28.21β	2α	—	265–267	5	*Stryphnodendron coriaceum*	92
Isoglabrolide	29.18α	—	11	318–325 (dec.)	46	*Glycyrrhiza glabra*	93
21α-Hydroxyisoglabrolide	29 18α	21α	11	304–305	−11 P	*Glycyrrhiza glabra*	38
Deoxyglabrolide	30.22β	—	—	274–278	60	*Glycyrrhiza glabra*	94
Glabrolide	30 22β	—	11	360–365 (dec.)	77	*Glycyrrhiza glabra*	94

* Unreliable as a method of identification. Similar data for a number of derivatives should also be sought

† For chloroform solutions except when marked as follows: A—acetone; D—dioxan; E—ethanol; M—methanol; P—pyridine.

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TABLE 2. ARTEFACTS OF β-AMYRIN TRITERPENOIDS

Precursor (function affected)	Artefact (function produced)	Ref.
Saikogenin E (11-en-13β,28-epoxy)	Saikogenin B (9(11),12-dien-28-ol)	19
	Saikogenin C (11,13(18)-dien-28-ol)	19
Saikogenin F (11-en-13β,28-epoxy)	Saikogenin A (11,13(18)-dien-28-ol)	19
Saikogenin G (11-en-13β,28-epoxy)	Saikogenin D (11,13(18)-dien-28-ol)	19
Protoprimulagenin A (13β,28-epoxy)	Primulagenin A (12-en-28-ol)	7
Cyclamiretin A (13β,28-epoxy)	Cyclamiretin D (12-en-28-ol)	45
	Cyclamigenins A^1 and C? (see Ref.)	46
Cyclamigenin B (30-al)	Cyclamigenins A^2 and D? (see Ref.)	46
Gypsogenin (12-en-28-oic acid)	Gypsogenin lactone (28:13β-lactone)	95
Stryphnodendron sapogenin B (28:21β-lactone)	Machaerinic acid (21β-ol-28-oic acid)	62,92
Stryphnodendron sapogenin F (28:21β-lactone)	Stryphnodendron sapogenin K (21β-ol-28-oic acid)	62,92
Protobassic acid (6β-ol)	Bassic acid (5-ene)	64
Barringtogenol C (16α,21β-diol)	Barringtogenol D = Jegosapogenol B (16α,21α-epoxy)	96
Protoaescigenin (16α,21β-diol)	Aescigenin (16α,21α-epoxy)	96
	Isoaescigenin (15-en-21α-ol)	96
Primulagenin A (16α-ol)	Aegiceradiol (15-ene)	97
	Aegiceradienol (28-*nor*-17(18)-ene)	97
?	Albigenin	98
Echinocystic acid (12-ene)	Albigenic acid (13(18)-ene)	82
Quillaic acid (12-ene)	— (13(18)-ene)	82
Theasapogenol E (23-al)	Camelliagenin D (24-al)	24
Presenegenin (12-en-27-ol)	Senegenin = Tenuifolic acid (27-*nor*-13(14)-ene-12α-chloromethyl)	85
	Senegenic acid = Polygalic acid (27-*nor*-13(14)-ene)	85
	Hydroxy-senegenin (27-*nor*-13(14)-ene-12α-hydroxymethyl)	85

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TABLE 3. DISTRIBUTION OF OXYGEN FUNCTIONS WITHIN NATURALLY OCCURRING 3β-HYDROXYOLEAN-12-ENES AND 3β-HYDROXY-13β,28-EPOXYOLEANANES†

Position	Functional group: Hydroxyl α	Hydroxyl β	Carbonyl	Carboxyl	% of compounds oxygenated at each position: Acids*	Non-acids	All
1	—	—	1		1·5	—	0·9
2	9	13	–		30·3	4·5	20·0
5	—	—	–		—	—	—
6	—	4	–		4·5	2·3	3·6
7	1	1	–		1·5	2·3	1·8
9	—	—	–		—	—	—
11	1	—	9		12·1	4·5	9·1
15	4	2	–		6·1	4·5	5·5
16	27	15	3		22·7	68 0	41·0
18	3	—	–		4·5	—	2·7
19	2	2	–		6 1	—	3·6
21	4	19	3		19·7	29·5	23·6
22	20	5	–		10·6	40·8	22·7
23	22		4	6	30·3	27·3	29·0
24	12		1	2	13 6	13·6	13 6
25	—		–	—	—	—	—
26	—		–	—	—	—	—
27	1		–	2	4·5	—	2·7
28	33		4	50	78 9	79·5	79·0
29	1		–	7	12·1	—	7·3
30	3		2	10	18·2	6·8	13·6

* Including lactones.
† 13β,28-epoxy = 28-hydroxy; lactones = hydroxy-acids.