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# Saponin and Sapogenol. XLI.[1] Reinvestigation of the Structures of Soyasapogenols A, B, and E, Oleanene-Sapogenols from Soybean. Structures of Soyasaponins I, II, and III

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A full account of the structure revision of soyasapogenols is presented. The structures of soyasapogenols A, B, and E have been confirmed to be expressed as 3β,21β,22β,24-tetrahydroxyolean-12-ene (**1**), 3β,22β,24-trihydroxyolean-12-ene (**2**), and 3β,24-dihydroxyolean-12-en-22-one (**5**), respectively, rather than the previously reported 3β,21α,22α,24-tetrahydroxyolean-12-ene (**1′**), 3β,21α,24-trihydroxyolean-12-ene (**2′**), and 3β,24-dihydroxyolean-12-en-21-one (**5′**). In consequence, the structures of soyasaponins I, II, and III are formulated as 3-*O*-[α-L-rhamnopyranosyl(1→2)-β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl]soyasapogenol B (**8**), 3-*O*-[α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranosyl(1→2)-β-D-glucuronopyranosyl]soyasapogenol B (**9**), and 3-*O*-[β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl]soyasapogenol B (**10**), respectively.

**Keywords**——soybean; *Glycine max*; oleanene-sapogenol; soyasapogenol A; soyasapogenol B; soyasapogenol E; soyasaponin I; soyasaponin II; soyasaponin III; bioactive triterpene oligoglycoside

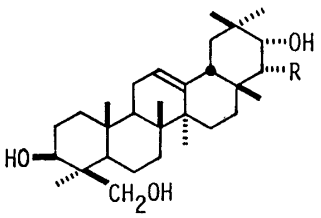
Soyasapogenols A, B, C, and D were isolated as sapogenols from soybean (*Glycine max* MERRILL., seeds) by Ochiai, Tsuda, and Kitagawa,[3] and structural investigations followed.[4] It was in 1958 when Smith *et al.* reported the structures of soyasapogenols A, B, and C as **1′**, **2′**, and **3**, respectively.[5] On the other hand in the same year, Cainelli *et al.* reported the structures of soyasapogenols C and D as **3** and **4**, and based on evidence obtained during the structural study, they commented that soyasapogenol B should contain a 22β-hydroxyl moiety in ring E, rather than having the hitherto proposed structure (**2′**) with a 21α-hydroxyl group.[6] However, probably because unestablished structures such as **1″** and **2″** were depicted for soyasapogenols A and B in their paper,[6] **1′**, **2′**, **3**, and **4** were generally accepted as the structures of soyasapogenols A, B, C, and D for a long period.[7] Afterwards, Willner *et al.* isolated a minor sapogenol named soyasapogenol E from soybean and reported its structure as **5′** on the basis of the chemical correlation with soyasapogenol B (**2′**).[8]

As a continuation of our chemical investigations on the bioactive principles in leguminous medicinal plants,[1,9] we have analyzed the chemical constituents of soybeans of various origins. From Japanese soybean (cultivated in Akita Prefecture), we isolated five bioactive triterpene-oligoglycosides, namely soyasaponins I, II, and III (having soyasapogenol B as the aglycone), and soyasaponins $A_1$ and $A_2$ (having soyasapogenol A as the aglycone).[10] We initially investigated the oligosaccharide moieties of soyasaponins I, II, and III and reported the whole structures of soyasaponins I, II, and III in which the sapogenol moieties were expressed on the basis of the previously reported structure (**2′**)[5] of soyasapogenol B.[11]

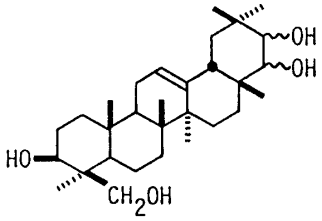
In 1982, Chiang *et al.* isolated soyasapogenols A and B, sophoradiol (**6**), and

cantoniensistriol (**7**) from the leguminous plant *Abrus cantoniensis* HANCE and elucidated the structures of **6** and **7** by X-ray analysis.[12] In the same report, they suggested that soyasapogenol A may have 21$\beta$,22$\beta$-hydroxyl groups rather than the previously believed 21$\alpha$,22$\alpha$-hydroxyls (**2'**) since it was contained with cantoniensistriol (**7**) in the same plant.

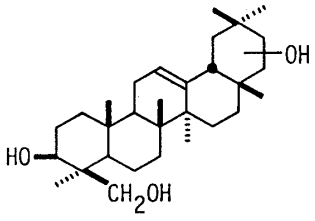
During the course of chemical conversion studies of glucuronide-saponins[13] and structure studies of soyasaponins $A_1$ and $A_2$,[14] we noticed that the structures (**1'**, **2'**) proposed for soyasapogenols A and B seemed inadequate. We therefore carried out a reinvestigation of soyasapogenols and we have reached the conclusion that the structures of soyasapogenols A, B, and E should be expressed as **1**, **2**, and **5** rather than as **1'**, **2'**, and **5'**, and consequently, the structures of soyasaponins I, II, and III should be formulated as **8**, **9**, and **10**, respectively.[15]



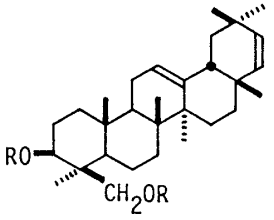
**1'** : R = OH
**2'** : R = H



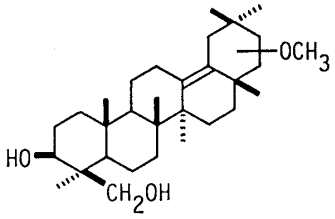
**1''**



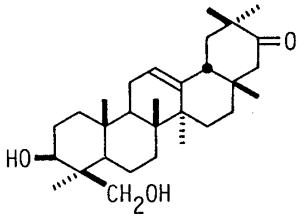
**2''**



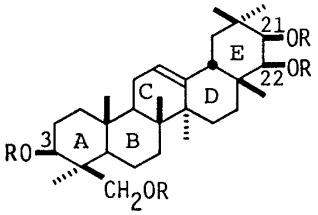
**3** ( soyasapogenol C )
: R = H
**3a** : R = Ac



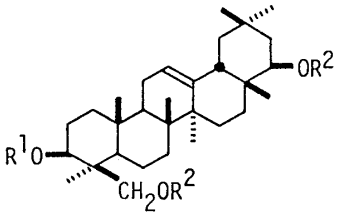
**4** ( soyasapogenol D )



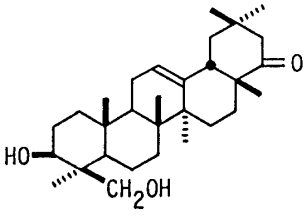
**5'**



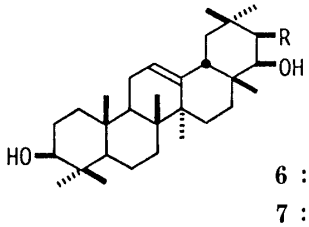
**1** ( soyasapogenol A )
: R = H
**1a** : R = Ac



**2** ( soyasapogenol B )
: $R^1 = R^2 = H$
**2a** : $R^1 = R^2 = Ac$
**2b** : $R^1 = R^2 = CH_3$
**2c** : $R^1 = H$, $R^2 = CH_3$



**5** ( soyasapogenol E )



**6** : R = H
**7** : R = OH

Chart 1

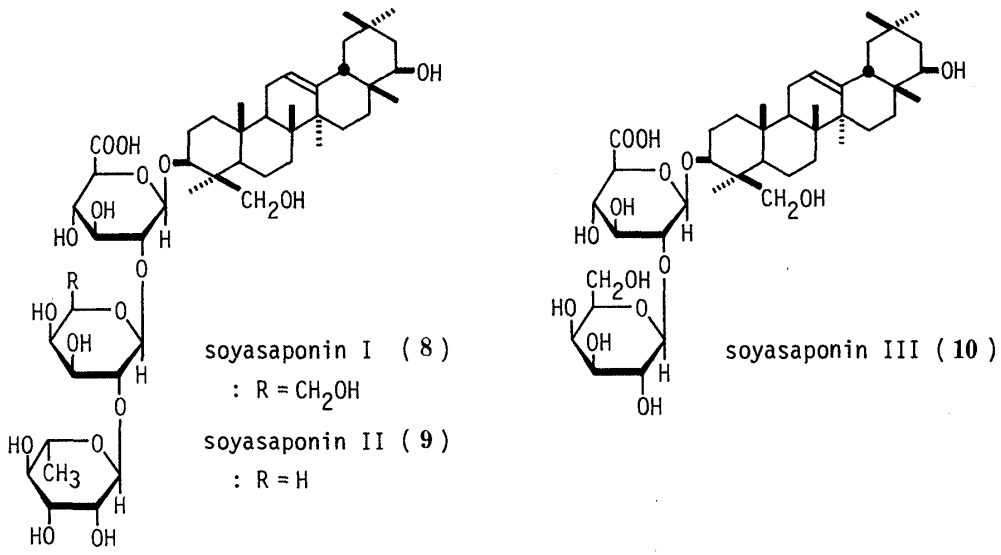



Chart 2

**Soyasapogenol B (2) and Soyasapogenol E (5)**

Irradiation of di-*O*-acetylsoyasapogenol E (**5a**), which was prepared from soyasapogenol B (**2**),[8] in a methanol–chloroform mixture in a Pyrex tube with a 500 W high-pressure mercury lamp furnished a seco-acid methyl ester (**11a**) in 85% yield. The proton nuclear magnetic resonance ($^1$H-NMR) spectrum of **11a** showed signals due to 3α-H, 24-$CH_2$, and six *tert*-$CH_3$ groups, a three-proton doublet ($J$=7.1 Hz) at $\delta$0.86 assignable to 17-*sec*-$CH_3$, and an AB quartet (2H, $J$=11.7 Hz) at $\delta$2.16 and 2.28 assignable to 21-$CH_2$. The mass spectrum (MS) of **11a** gave the molecular ion peak and two fragment ions **i** and **iii** formed through a retro-Diels–Alder type fragmentation characteristic of the C-ring fragmentation of olean-12-ene triterpenoids.[16] Irradiation of di-*O*-acetylsoyasapogenol E (**5a**) in chloroform without methanol provided a seco-acid (**11**) in 81% yield.[17] The $^1$H-NMR spectrum of **11** also showed signals due to six *tert*-$CH_3$ and one *sec*-$CH_3$ groups.

Selenium dioxide oxidation of **11a** gave a dienic compound (**12a**), which was converted to the dienic acid (**12**) by methanolic sodium methoxide treatment. The ultraviolet (UV) spectra of **12** and **12a** showed absorption curves which were reminiscent of an 11,13(18)-heteroannular diene moiety.[13c,18] In addition, the $^1$H-NMR spectrum showed signals due to two olefinic protons at C-11 and C-12 (in **12** and **12a**)[13c,18] and a doublet due to 17-$CH_3$ (in **12**).[19]

Based on the above-mentioned evidence, the location of the carbonyl moiety in soyasapogenol E (**5**) has been proved to be C-22 and the photolysis of **5a** resulted in C-17, 22-bond fission (α-fission) to provide **11a** and **11**. Therefore, the location of the hydroxyl moiety in ring E of soyasapogenol B (**2**) has been shown to be at C-22. Furthermore, the $^1$H-NMR spectra of **2a**,[20] **2b**,[20] **2c**,[11] **21**, and **22** (*vide infra*) indicated the axial orientation of the 22-hydroxyl group as judged from the signal due to 22-H. Thus, the structure of soyasapogenol B (**2**) has been elucidated to be as shown.

In order to confirm the new structure of soyasapogenol B (**2**), the conversion of **2** to sophoradiol (**6**)[12] has been carried out. Tritylation of **2** gave the monotrityl ether (**13**), which was then treated with phenyl isocyanate to afford the phenylcarbamate (**14**). Detritylation of **14** (giving **15**) and subsequent oxidation of **15** with pyridinium chlorochromate (PCC) yielded the aldehyde (**16**). Huang–Minlon reduction of **16**, with concomitant removal of the protecting group, provided the 24-deoxy product (in 32% overall yield from **2**), which was found to be identical with sophoradiol (**6**).

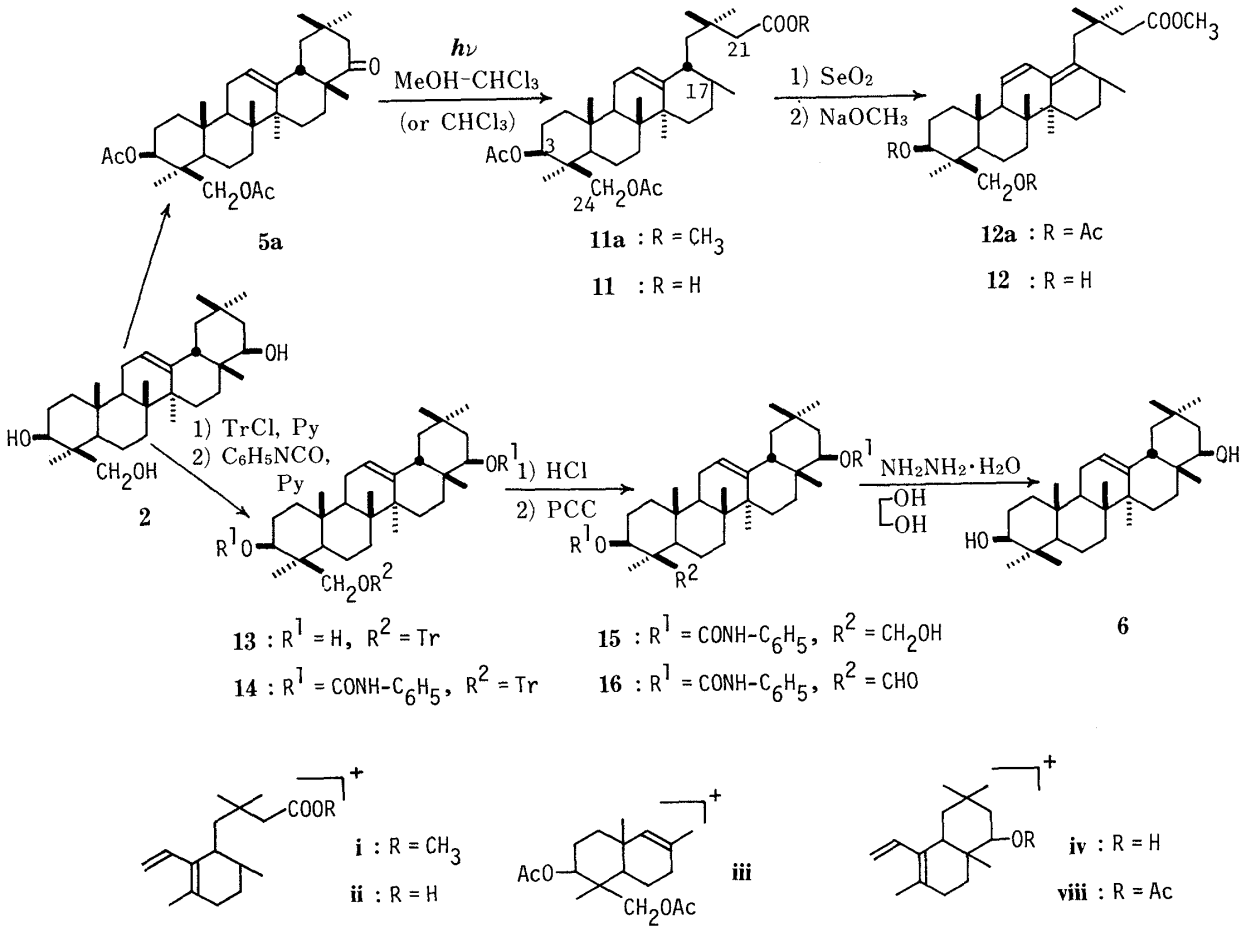



Chart 3

Furthermore, the X-ray analysis of 3,22,24-tri-*O*-acetylsoyasapogenol B (**2a**) confirmed the structure of soyasapogenol B (**2**),[15] and consequently the structure of soyasapogenol E (**5**) has been determined to be as shown. Based on the confirmed evidence previously reported[11] and mentioned above, the structures of soyasaponins I, II, and III, which are oligoglycosides of soyasapogenol B (**2**), should be expressed as **8**, **9**, and **10**, respectively.

**Soyasapogenol A (1)**

Soyasapogenol B (**2**) was previously correlated to tetra-*O*-acetylsoyasapogenol A (**1a**) *via* initial conversion of **2a** to di-*O*-acetylsoyasapogenol C (**3a**) and subsequent osmium tetroxide oxidation followed by acetylation.[4,5] We repeated these conversions and have found that they are reproducible. It has become clear therefore that if the configuration of one of the two hydroxyl groups at C-21 and C-22 in soyasapogenol A (**1**) is determined, the chemical structure of soyasapogenol A will be elucidated. Thus, the conversion from soyasapogenol A (**1**) to a soyasapogenol B derivative (**20**) has been carried out.

Treatment of soyasapogenol A (**1**) with 2,2-dimethoxypropane (one equiv. mol excess) in the presence of acidic resin in acetone, furnished the 21-*O*-,22-*O*-isopropylidene derivative (**17**). Methylation of **17** with methyl iodide and sodium hydride in tetrahydrofuran (THF) gave the 3,24-di-*O*-methyl ether (**18**) (in 70% yield from **1**). The MS of **17** and **18** showed a base-ion peak **v** derived from their D, E rings, so that the location of the 21-*O*-,22-*O*-isopropylidene group has been ascertained. Removal of the isopropylidene protecting group of **18** with acid and subsequent acetylation under ordinary conditions provided the 21-*O*-acetate (**19**) in 75% yield. The $^1$H-NMR spectrum of **19** showed signals due to 3α-H and 24-

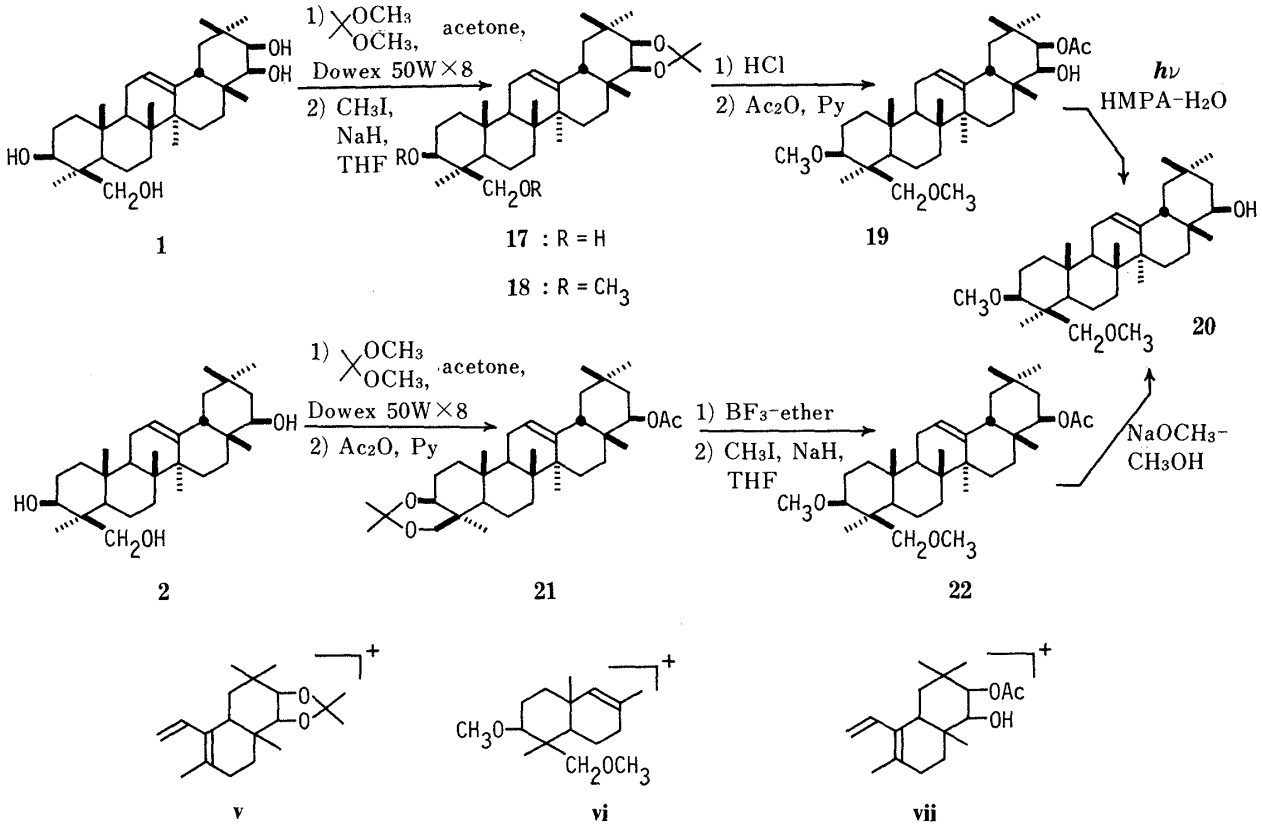



Chart 4

$CH_2$, a one-proton doublet at $\delta$3.44 ($J$=2.4 Hz) assignable to 22$\alpha$-H, and a one-proton doublet at $\delta$4.94 ($J$=2.4 Hz) assignable to 21$\alpha$-H. Irradiation of **19** in a hexamethylphosphoric triamide (HMPA)–water (95 : 5) mixture in a quartz tube with a 30 W low-pressure mercury lamp,[21] furnished the 21-deacetoxylated product (**20**) in 81% yield.

On the other hand, isopropylidenation followed by acetylation of soyasapogenol B (**2**) gave **21**. Removal of the isopropylidene moiety from **21** with boron trifluoride etherate and subsequent methylation of the product gave **22**. Finally, deacetylation of **22** with methanolic sodium methoxide furnished 3,24-di-*O*-methylsoyasapogenol B in 73% overall yield from soyasapogenol B (**2**). The di-*O*-methyl ether thus obtained was found to be identical with **20** described above. Thus, the 22-OH configuration of soyasapogenol A (**1**) has been proved to be $\beta$, as in soyasapogenol B (**2**), and the structure of soyasapogenol A has been determined to be 3$\beta$,21$\beta$,22$\beta$,24-tetrahydroxyolean-12-ene (**1**).

Very recently, we have analyzed the saponin constituents in a variety of soybeans cultivated in various places in Japan and imported from the United States of America, Canada, and China. We have found so far that soyasaponins having soyasapogenols A (**1**) and B (**2**) as the aglycones are contained in soybeans as partially acetylated forms.[22,23] Furthermore, it has been found that soyasapogenols C (**3**) and D (**4**) are artifacts secondarily formed during the acidic hydrolysis of soyasaponins, whereas soyasapogenol E (**5**) may be formed by photo-oxidation of soyasapogenol B (**2**).[22,24] Soyasapogenols A (**1**) and B (**2**) described in this paper are genuine sapogenols of soybean.

## Experimental[25]

**Photolysis of 5a**——a) A solution of **5a** (50 mg) in $CHCl_3$–MeOH (1 : 1, 16 ml) in a Pyrex tube was irradiated

externally with a 500 W high-pressure mercury lamp (Eikosha, PIH-500) for 2.5 h while keeping the solution temperature below 4 °C. After removal of the solvent from the reaction mixture under reduced pressure, the product was purified by preparative thin layer chromatography (TLC) (benzene : acetone = 5 : 1) and crystallization from MeOH to furnish **11a** (45 mg, 85%). **11a**, mp 162—163 °C (colorless needles), $[\alpha]_D^{20}$ +69.1° ($c$ = 1.0, $CHCl_3$). High-resolution MS: Found: 572.408, 264.207, 248.176. Calcd for $C_{35}H_{56}O_6$ ($M^+$): 572.408, $C_{17}H_{28}O_2$ (**i**): 264.209, $C_{16}H_{24}O_2$ (**iii**-AcOH): 248.178. IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 2945, 1737, 1233. $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$: 0.86 (3H, d, $J$ = 7.1 Hz, changed to s on irradiation at $\delta$ 1.65, 17-*sec* $-CH_3$), 0.94, 0.98, 0.99, 1.01, 1.02, 1.05 (3H each, all s, *tert* $-CH_3 \times 6$), 2.04, 2.06 (3H each, both s, OAc × 2), 2.16, 2.28 (2H, ABq, $J$ = 11.7 Hz, 21-$H_2$), 3.65 (3H, s, $COOCH_3$), 4.13, 4.37 (2H, ABq, $J$ = 11.7 Hz, 24-$H_2$), 4.59 (1H, dd, $J$ = 7.1, 9.3 Hz, 3-H), 5.25 (1H, dd, $J$ = 3.2, 3.2 Hz, 12-H). $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$: 0.85, 0.96, 1.03, 1.07, 1.08, 1.16 (3H each, all s, *tert* $-CH_3 \times 6$), 0.95 (3H, d, $J$ = 7.2 Hz, *sec* $-CH_3$), 1.70, 1.74 (3H each, both s, OAc × 2), 2.19, 2.20 (2H, ABq, $J$ = 14.4 Hz, 21-$H_2$), 3.36 (3H, s, $COOCH_3$), 4.20, 4.59 (2H, ABq, $J$ = 11.8 Hz, 24-$H_2$), 4.71 (1H, dd, $J$ = 7.1, 9.2 Hz, 3-H), 5.30 (1H, dd, $J$ = 3.2, 3.2 Hz, 12-H). $^{13}$C-NMR (50 MHz, $CDCl_3$)[26] $\delta_c$: 15.7, 17.0, 19.4, 21.1, 21.2, 22.6, 23.0, 26.9 (2C) (*tert* $-CH_3 \times 6$, *sec* $-CH_3$, acetyl-$CH_3 \times 2$), 19.3, 23.2, 23.7 (3C), 33.8, 38.7, 46.4, 51.7 ($-CH_2- \times 9$), 33.2, 44.6, 47.7, 56.1 (>CH × 4), 34.7, 36.8, 39.4, 41.1, 43.0 (>C< × 5), 51.0 ($OCH_3$), 65.5 (24-C), 80.2 (3-C), 122.2 (11-C), 143.7 (12-C), 170.5, 170.9 (acetyl-CO × 2), 172.7 (22-C). MS $m/z$ (%): 572 ($M^+$, 85), 308 (**iii**, 4), 264 (**i**, 86), 248 (**iii**-AcOH, 22).

b) A solution of **5a** (50 mg) in $CHCl_3$ (10 ml) in a Pyrex tube was irradiated externally with a 500 W high-pressure mercury lamp for 2.5 h while keeping the solution temperature below 4 °C. The product, obtained by evaporation of the solvent under reduced pressure, was purified by preparative TLC (benzene : acetone = 2 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish **11** (42 mg, 81%). **11**, mp 176—178 °C (colorless needles), $[\alpha]_D^{20}$ +74.3° ($c$ = 0.35, $CHCl_3$). High-resolution MS: Found: 558.394, 250.192, 248.175. Calcd for $C_{34}H_{54}O_6$ ($M^+$): 558.392, $C_{16}H_{26}O_2$ (**ii**): 250.193, $C_{16}H_{24}O_2$ (**iii**-AcOH): 248.178. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 2960, 1755 (br), 1280. $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$: 0.87 (3H, d, $J$ = 7.2 Hz, 17-*sec* $-CH_3$), 0.94, 0.98, 1.02, 1.03 (3H each), 1.05 (6H) (all s, *tert* $-CH_3 \times 6$), 2.04, 2.07 (3H each, both s, OAc × 2), 2.19, 2.29 (2H, ABq, $J$ = 12.0 Hz, 21-$H_2$), 4.13, 4.36 (2H, ABq, $J$ = 11.8 Hz, 24-$H_2$), 4.59 (1H, t-like, 3-H), 5.25 (1H, br s, $W_{h/2}$ = 6 Hz, 12-H). MS $m/z$ (%): 558 ($M^+$, 7), 250 (**ii**, 24), 248 (**iii**-AcOH, 5).

**$SeO_2$ Oxidation of 11a**——A solution of **11a** (180 mg) in AcOH (10 ml) was treated with $SeO_2$ (200 mg), and the mixture was heated under reflux for 1 h. The reaction mixture was then poured into ice-water and the precipitated product was collected by filtration. The product was purified by column chromatography ($SiO_2$ 5 g, $CHCl_3$) and subsequent crystallization from MeOH to furnish **12a** (150 mg, 84%). **12a**, mp 115—116 °C (colorless needles), $[\alpha]_D^{20}$ −0.9° ($c$ = 0.3, $CHCl_3$). High-resolution MS: Found 570.391. Calcd for $C_{35}H_{54}O_6$ ($M^+$): 570.392. UV $\lambda_{max}^{MeOH}$ nm ($\varepsilon$): 245 (33000), 253 (37000), 261 (24000). IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 2965, 1725, 1250. $^1$H-NMR (90 MHz, $CDCl_3$)[27] $\delta$: 0.74 (3H, s), 0.96—1.00 (18H) (*tert* $-CH_3 \times 6$, *sec* $-CH_3$), 2.02, 2.04 (3H each, both s, OAc × 2), 2.24 (2H, s, 21-$H_2$), 3.65 (3H, s, $COOCH_3$), 4.11, 4.33 (2H, ABq, $J$ = 10 Hz, 24-$H_2$), 4.60 (1H, t-like, 3-H), 5.44 (1H, d, $J$ = 10 Hz, 11-H), 6.33 (1H, dd, $J$ = 3, 10 Hz, 12-H). MS $m/z$ (%): 570 ($M^+$, 70), 201 (100).

**Deacetylation of 12a**——A solution of **12a** (100 mg) in MeOH (20 ml) was treated with 10% NaOMe–MeOH (1 ml) and the mixture was stirred at 20 °C for 1 h. The reaction mixture was then neutralized with Dowex 50W × 8 ($H^+$ form) and the resin was removed by filtration. Concentration of the filtrate under reduced pressure yielded **12** (85 mg, quant.). **12**, a white powder, $[\alpha]_D^{20}$ −6.0° ($c$ = 1.5, $CHCl_3$). High-resolution MS: Found 486.371. Calcd for $C_{31}H_{50}O_4$ ($M^+$): 486.371. UV $\lambda_{max}^{MeOH}$ nm ($\varepsilon$): 247 (36700), 253 (41100), 263 (26700). IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3620, 3500, 1725, 1025. $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$: 0.71, 0.85, 0.95, 0.99, 1.01, 1.24 (3H each, all s, *tert* $-CH_3 \times 6$), 0.98 (3H, d, $J$ = 7.1 Hz, 17-*sec* $-CH_3$), 2.24 (2H, s), 3.66 (3H, s, $COOCH_3$), 5.46 (1H, d, $J$ = 11.2 Hz, 11-H), 6.33 (1H, dd, $J$ = 2.0, 11.2 Hz, 12-H). MS $m/z$ (%): 486 ($M^+$, 100), 201 (53).

**Tritylation of Soyasapogenol B (2)**——A solution of **2** (2.85 g) in pyridine (75 ml) was treated with trityl chloride (4.5 g) and the mixture was heated under reflux for 0.5 h. The reaction mixture was then poured into ice-water and the precipitated product was collected by filtration. The product was purified by column chromatography ($SiO_2$ 400 g, $n$-hexane : AcOEt = 15 : 1—1 : 1, $CHCl_3$) followed by crystallization from $n$-hexane–AcOEt to furnish **13** (3.84 g, 88%). **13**, mp 293—294 °C (colorless needles), $[\alpha]_D^{12}$ +72.5° ($c$ = 0.5, pyridine). *Anal.* Calcd for $C_{49}H_{64}O_3$: C, 83.95; H, 9.20. Found: C, 83.84; H, 9.46. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3470, 3430, 1600, 1495. MS $m/z$ (%): 700 ($M^+$, 1), 243 (100), 234 (**iv**, 70).

**Phenylcarbamate (14) Formation from 13**——A solution of **13** (3.74 g) in pyridine (50 ml) was treated with phenylisocyanate (1.2 ml) and the mixture was heated at 100 °C for 1 h. The reaction mixture was then poured into ice-water and the whole was extracted with AcOEt. After work-up of the AcOEt extract in the usual manner, the product was purified by column chromatography ($Al_2O_3$ 50 g, $n$-hexane : AcOEt = 1 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish **14** (4.41 g, 88%). **14**, mp 157—159 °C (colorless plate), $[\alpha]_D^{13}$ +5.5° ($c$ = 0.47, $CHCl_3$). *Anal.* Calcd for $C_{63}H_{74}O_5N_2$: C, 80.56; H, 7.94; N, 2.98. Found: C, 80.82; H, 7.82; N, 2.92. IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 3440, 3065, 3025, 1740, 1515. $^1$H-NMR ($CDCl_3$) $\delta$: 0.86 (9H), 0.91, 1.01, 1.13, 1.31 (3H each) (all s, *tert* $-CH_3 \times 7$), 3.13, 3.43 (2H, ABq, $J$ = 8.5 Hz, 24-$H_2$), 4.46—4.64 (2H, m, 3, 22-H), 5.18 (1H, m, 12-H), 6.35, 6.59 (1H each, both s, >NH × 2), 7.10—7.50 (25H, m, aromatic H).

**Detritylation of 14**——A solution of **14** (4.9 g) in MeOH–acetone (5 : 1, 120 ml) was treated with concentrated HCl (4 ml) and the mixture was heated under reflux for 20 min. After neutralization with 5% aqueous NaOH, the

whole mixture was poured into ice-water and the precipitated product was collected by filtration. The product was purified by column chromatography ($SiO_2$ 200 g, *n*-hexane : AcOEt = 5 : 1—1 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish **15** (3.6 g, quant.). **15**, mp 288—290 °C (colorless fine crystals), $[\alpha]_D^{12}$ +83.3° (*c* = 1.1, pyridine). *Anal.* Calcd for $C_{44}H_{60}O_5N_2$: C, 75.83; H, 8.68; N, 4.02. Found: C, 75.45; H, 8.75; N, 4.00. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3600, 3350, 1730, 1550. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.92 (3H), 0.95 (9H), 1.04, 1.19, 1.33 (3H each) (all s, *tert* –$CH_3$ × 7), 3.94 (2H, br s, 24-$H_2$), 5.24 (1H, br s, 12-H), 7.00—8.03 (10H, m, aromatic H).

**PCC Oxidation of 15**——A solution of **15** (100 mg) in $CH_2Cl_2$ (10 ml) was treated with PCC (100 mg) and the mixture was stirred at 20 °C under a nitrogen atmosphere for 2.5 h. The product was purified by column chromatography [Florisil (100—200 mesh) 1 g, ether] and preparative TLC (*n*-hexane : AcOEt = 2 : 1) to furnish **16** (71 mg, 71%). **16**, a white powder $[\alpha]_D^{12}$ +81.1° (*c* = 1.1, pyridine). *Anal.* Calcd for $C_{44}H_{58}O_5N_2$: C, 76.05; H, 8.41; N, 4.03. Found: C, 75.73; H, 8.41; N, 4.13. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3340, 2830, 2740, 1705, 1515. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.78, 0.82 (3H each), 0.90 (9H), 1.19, 1.23 (3H each) (all s, *tert* –$CH_3$ × 7), 5.19 (1H, br s, 12-H), 7.10—8.05 (10H, m, aromatic H), 10.15 (1H, s, –CHO).

**Huang-Minlon Reduction of 16**——A solution of **16** (130 mg) in EtOH (30 ml) was treated with diethylene glycol (15 ml) and 80% hydrazine hydrate (5 ml) and the mixture was heated at 140—150 °C (in an oil bath) for 2 h. The reaction mixture was then treated with KOH (1.5 g) and the whole mixture was heated under reflux (230—240 °C) for a further 3 h, poured into ice-water and extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by preparative TLC (benzene : acetone = 10 : 1) to furnish sophoradiol (**6**, 48 mg). Sophoradiol (**6**) thus obtained was shown to be identical with an authentic sample[28] by TLC ($CHCl_3$ : MeOH = 30 : 1, benzene : acetone = 4 : 1, *n*-hexane : AcOEt = 1 : 1), mixed melting point determination and IR (KBr) comparisons.

**Conversion from Soyasapogenol A (1) to the Monoacetonide (17)**——A solution of **1** (500 mg) in acetone (100 mg) was treated with 2,2-dimethoxypropane (2 ml) and dry Dowex 50W × 8 ($H^+$ form, 10 ml). The mixture was stirred at 20 °C for 24 h and the resin was removed by filtration. The product, obtained by concentration of the filtrate under reduced pressure, was purified by column chromatography ($Al_2O_3$ 25 g, benzene : acetone = 10 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish **17** (380 mg, 70%). **17**, mp 268—269 °C (colorless fine crystals), $[\alpha]_D^{20}$ +88.8° (*c* = 1.0, $CHCl_3$). High-resolution MS: Found 514.402. Calcd for $C_{33}H_{54}O_4$ ($M^+$): 514.402. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3500, 1385, 1040. $^1$H-NMR ($CDCl_3$) $\delta$: 0.91, 0.96 (6H, each), 0.99, 1.11, 1.24 (3H each) (all s, *tert* –$CH_3$ × 7), 1.34, 1.37 (3H each, both s, isopropylidene–$CH_3$ × 2), 3.29, 4.17 (2H, ABq, *J* = 11 Hz, 24-$H_2$), 3.70 (2H, s, 21, 22-H), 5.22 (1H, t-like, 12-H). MS *m/z* (%): 514 ($M^+$, 1), 290 (**v**, 100).

**Methylation of 17**——A solution of **17** (200 mg) in THF (5 ml) was mixed with $CH_3I$ (2 ml) and NaH (200 mg), and the mixture was stirred at 20 °C under a nitrogen atmosphere for 10 h. After quenching of the reaction with wet ether, the reaction mixture was poured into ice-water and extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by column chromatography ($SiO_2$ 15 g, $CHCl_3$) and crystallization from $CHCl_3$–MeOH to furnish **18** (210 mg, quant.). **18**, mp 239—240 °C (colorless needles), $[\alpha]_D^{20}$ +120.6° (*c* = 1.0, $CHCl_3$). High-resolution MS: Found 542.435. Calcd for $C_{35}H_{58}O_4$ ($M^+$): 542.433. IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 2950, 1045. $^1$H-NMR ($CDCl_3$) $\delta$: 0.91 (3H), 0.97, 0.99, 1.11 (6H each) (all s, *tert* –$CH_3$ × 7), 1.32, 1.46 (3H each, both s, isopropylidene–$CH_3$ × 2), 2.69 (1H, dd, *J* = 3, 8 Hz, 3-H), 3.23, 3.31 (3H each, both s, $OCH_3$ × 2), 3.70 (2H, s, 21, 22-H), 5.23 (1H, t-like, 12-H). MS *m/z* (%): 542 ($M^+$, 1), 290 (**v**, 100), 252 (**vi**, 12).

**Conversion from 18 to 19**——A solution of **18** in THF (10 ml) was treated with 5% aqueous HCl (1 ml) and the mixture was stirred at 20 °C for 1 h. The reaction mixture was neutralized with 5% aqueous NaOH and the whole was extracted with ether. Work-up of the ether extract in the usual manner gave the product, which was dissolved in $Ac_2O$–pyridine (1 : 1, 5 ml). This solution was stirred at 20 °C for 6 h, then poured into ice-water, and the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by column chromatography ($SiO_2$ 10 g, *n*-hexane : AcOEt = 10 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish **19** (128 mg, 75%) and to recover **18** (30 mg). **19**, mp 229—230 °C (colorless needles), $[\alpha]_D^{20}$ +95.7° (*c* = 0.6, $CHCl_3$). High-resolution MS: Found 544.412. Calcd for $C_{34}H_{56}O_5$ ($M^+$): 544.413. IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 3610, 1740, 1240, 1050. $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$: 0.85, 0.96, 0.98, 0.99 (3H each), 1.12 (6H), 1.14 (3H) (all s, *tert* –$CH_3$ × 7), 2.13 (3H, s, OAc), 2.72 (1H, dd, *J* = 4.1, 11.0 Hz, 3-H), 3.26, 3.34 (3H each, both s, $OCH_3$ × 2), 3.30, 3.54 (2H, ABq, *J* = 9.8 Hz, 24-$H_2$), 3.44 (1H, d, *J* = 2.4 Hz, changed to s on irradiation at $\delta$ 4.94, 22-H), 4.94 (1H, d, *J* = 2.4 Hz, changed to s on irradiation at $\delta$ 3.44, 21-H), 5.27 (1H, t-like, 12-H). MS *m/z* (%): 544 ($M^+$, 1), 292 (**vii**, 6), 252 (**vi**, 20), 232 (**vii**-AcOH, 100).

**Photolysis of 19**——A solution of **19** (100 mg) in HMPA–$H_2O$ (95 : 5, 40 ml) in a quartz tube was irradiated externally with a 30 W low-pressure mercury lamp (PIL-30) for 48 h while keeping the solution temperature below 10 °C. After dilution with water, the reaction mixture was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by column chromatography ($SiO_2$ 10 g, $CHCl_3$ : MeOH = 100 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish **20** (72 mg, 81%). **20**, mp 228—229 °C (colorless needles), $[\alpha]_D^{20}$ +92.9° (*c* = 1.0, $CHCl_3$). High-resolution MS: Found 486.407. Calcd for $C_{32}H_{54}O_3$ ($M^+$): 486.407. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3520, 2920, 1050. $^1$H-NMR ($CDCl_3$) $\delta$: 0.87, 0.90, 0.97, 1.00, 1.04 (3H each), 1.11 (6H) (all s, *tert* –$CH_3$ × 7), 2.70 (1H, dd, *J* = 4, 8 Hz, 3-H), 3.24, 3.32 (3H each, both s, $OCH_3$ × 2), 5.21 (1H, t-like, 12-H). MS *m/z*

(%): 486 ($M^+$, 5), 252 (**vi**, 22), 234 (**iv**, 100).

**Conversion from Soyasapogenol B (2) to 21**——A solution of **2** (375 mg) in acetone (25 ml) was treated with 2,2-dimethoxypropane (15 ml) and dry Dowex 50W × 8 ($H^+$ form, 10 ml). The mixture was stirred at 37 °C for 12 h and the resin was removed by filtration. The product, obtained by evaporation of the solvent from the filtrate under reduced pressure, was dissolved in $Ac_2O$–pyridine (1 : 1, 2 ml). This solution was stirred at 20 °C for 12 h, then poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by column chromatography ($SiO_2$ 20 g, benzene : acetone = 100 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish **21** (398 mg, 90%). **21**, mp 239—240 °C (colorless needles), $[\alpha]_D^{20}$ +86.1° ($c$ = 0.6, $CHCl_3$). High-resolution MS: Found 540.419. Calcd for $C_{35}H_{56}O_4$ ($M^+$): 540.420. IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 2950, 1730, 1250. $^1$H-NMR ($CDCl_3$) $\delta$: 0.82, 0.90 (3H each), 1.00, 1.16 (6H each), 1.22 (3H) (all s, *tert* –$CH_3$ × 7), 1.37, 1.42 (3H each, both s, isopropylidene–$CH_3$ × 2), 2.00 (3H, s, OAc), 3.20, 4.02 (1H each, both d, $J$ = 11 Hz, 24-$H_2$), 3.44 (1H, dd, $J$ = 3, 8 Hz, 3-H), 4.62 (1H, dd, $J$ = 3.5, 3.5 Hz, 22-H), 5.25 (1H, t-like, 12-H). MS $m/z$ (%): 500 ($M^+$, 2), 276 (**viii**, 20), 216 (**viii**-AcOH, 100).

**Conversion from 21 to 22**——A solution of **21** (180 mg) in THF (10 ml) was treated with $BF_3$–ether (0.1 ml) and the whole mixture was stirred at 20 °C for 5 min. The reaction mixture was neutralized with aqueous saturated $NaHCO_3$ and the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product. A solution of the product in THF (10 ml) was treated with $CH_3I$ (5 ml) and NaH (100 mg) and the mixture was stirred at 20 °C for 10 h. After quenching of the reaction with wet ether, the reaction mixture was poured into ice-water and extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by column chromatography ($SiO_2$ 25 g, $CHCl_3$ : MeOH = 500 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish **22** (158 mg, 83%). **22**, mp 209—210 °C (colorless needles), $[\alpha]_D^{20}$ +99.1° ($c$ = 0.5, $CHCl_3$). High-resolution MS: Found 528.419. Calcd for $C_{34}H_{56}O_4$ ($M^+$): 528.418. IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 2925, 1730, 1250. $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$: 0.81, 0.88, 0.97 (3H each), 1.00 (6H), 1.12, 1.13 (3H each) (all s, *tert* –$CH_3$ × 7), 2.01 (3H, s, OAc), 2.70 (1H, dd, $J$ = 4.1, 8.0 Hz, 3-H), 3.24, 3.32 (3H each, both s, $OCH_3$ × 2), 4.61 (1H, dd, $J$ = 3.5, 3.5 Hz, 22-H), 5.23 (1H, t-like, 12-H). MS $m/z$ (%): 528 ($M^+$, 7), 276 (**viii**, 26), 252 (**vi**, 21), 216 (**viii**-AcOH, 100).

**Deacetylation of 22**——A solution of **22** (20 mg) in MeOH (5 ml) was treated with 10% NaOMe–MeOH (1 ml) and the reaction mixture was stirred at 20 °C for 1 h, then neutralized with Dowex 50W × 8 ($H^+$ form). The resin was removed by filtration. Removal of the solvent from the filtrate under reduced pressure gave **20** (18 mg, quant.), which was shown to be identical with an authentic sample by TLC ($CHCl_3$, benzene : acetone = 15 : 1, *n*-hexane : AcOEt = 5 : 1), mixed melting point determination, and IR ($CHCl_3$) spectral comparison.

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25) The following instruments were used to obtain physical data: melting points, Yanagimoto micro-melting point apparatus (values are uncorrected); specific rotations, JASCO DIP-181 digital polarimeter ($l=0.5$ or 1 dm); IR spectra, Hitachi 260-30 infrared spectrometer; UV spectra, Hitachi 330 spectrophotometer; $^1$H-NMR spectra, JEOL FX-90Q (89.55 MHz) or JEOL FX-200 (200 MHz) FT NMR spectrometer (with tetramethylsilane as an internal standard); $^{13}$C-NMR spectra, JEOL FX-200 (50 MHz) FT NMR spectrometer; MS, JEOL JMS-new D-300 mass spectrometer; high-resolution MS, JEOL JMS-new D-300 or JEOL JMS-01SG mass spectrometer. The following experimental conditions were used for chromatography: gas liquid chromatography (GLC), Hitachi gas chromatograph model 663-50 with FID; column chromatography, Silica gel 60 (Merck, 60—230 mesh) or aluminum oxide standardized (Merck) as the adsorbent; preparative TLC, with silica gel Camag D-5, detection by spraying with water or by exposure to $I_2$ vapor; TLC, pre-coated TLC plates silica gel 60F-254 (0.25 mm), detection by spraying with 1% $Ce(SO_4)_2$–10% aqueous $H_2SO_4$ followed by heating.
26) The characterizations of *prim*-C, *sec*-C, *tert*-C and *quat*-C were based on INEPT (insensitive nuclei enhanced by polarization transfer) experiments.
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